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on Chemical Spills

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HERMES:
AN EXPERT SYSTEM FOR EMERGENCY RESPONSE MANAGEMENT

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Abstract

HERMES is an application of knowledge representation and reasoning techniques of expert systems in the area of the emergency management of spills of hazardous materials. Using incident case data, fundamental knowledge such as properties of chemicals, and experiential knowledge in managing chemical spills, the system makes risk estimates and suggests procedures for containment and corrective actions. HERMES includes a sophisticated interface to facilitate the communication between the user and the knowledge base. It has been prototyped in ART on the Symbolics Lisp machine and then ported to the PC using the PC-based AI development tool GoldWorks and the graphics package Halo. Further development is considered for a full production system.

Introduction

The area of emergency response management is realizing the potential of expert system technology as an integral part of day to day operations. In particular, the emergency response team at the Alberta Public Safety Services has initiated an undertaking in this direction with Emergency Preparedness Canada and the Alberta Research Council, the latter providing the expertise in expert systems technology. The result is a joint research work on the expert system called HERMES (Heuristic Emergency Response Management Expert System).

HERMES addresses two main problems faced by the response team in the management of an incident involving hazardous materials. First, there is the problem of analyzing a given situation and determining the nature of the crisis and any potential hazards. Then there is the task of deciding quick effective advice on how to best deal with the situation. In both of these activities, the following are the prevalent difficulties. It is noted that these are also the concerns that expert systems are shown to be useful for [2].

- Often, a decision must be made despite incomplete or inexact information.
- The volume and diversity of knowledge processed exceeds the capabilities of human experts.
- Human expertise is scarce and needs to be duplicated in many locations or for extended periods of time.

Hence, the area of emergency response management is a good candidate for the application of expert system techniques, and vice versa, expert system technology may have the answer to many of the pressing needs in emergency response management. This is evidenced by the promising results of the HERMES prototype as a system for facilitating the management of spills of hazardous materials. It can perform the two main activities for automated response management-hazard assessment and advice generation. As well, it is a useful tool in other aspects of emergency management such as personnel training and preservation of expertise. The following details the development of HERMES, together with an elementary treatment of expert system concepts.

The Emergency Response Process

In Alberta, consultation regarding emergency response is a service provided by the APSS Compliance Centre 24-hour hotline. Emergency personnel such as police and firemen at the scene of the incident phone in to describe the situation to the response team at the Compliance Centre. The response team takes these case data and consults different reference materials to make inferences and decisions regarding hazard assessment and countermeasure possiblities. The resulting evaluation and advice are then relayed back to the emergency personnel who will carry out the appropriate actions. The general emergency response process just described is pictured in Figure 1. Examples for each of the input and output components of the decision making process are given below.

- Case data include the chemical substance(s) involved, rate and volume of leakage, container type, container damage type, ambient weather conditions, population centres, bodies of water, and nearby traffic.
- Knowledge base contains fundamental knowledge such as human exposure limits, fire and explosive limits, phase changes and other properties of chemicals; and heuristic knowledge such as those for estimating evacuation distance based on substance flammability and fire type.
- Hazard assessment includes estimates of fire potential and explosion potential, immediate injury to emergency personnel and the public, and long term effects to humans and the environment.

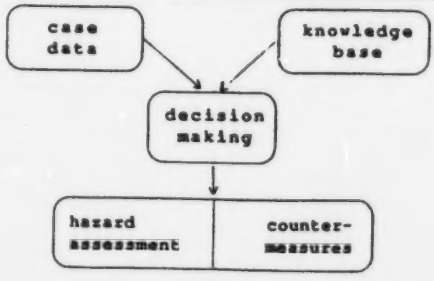

Figure 1. Structure of Emergency Response Process

- Countermeasures include recommended evacuation distance and direction, advice for appropriate clothing and breathing apparatus, procedures for leak and fire containment, and procedures for the subsequent clean-up.

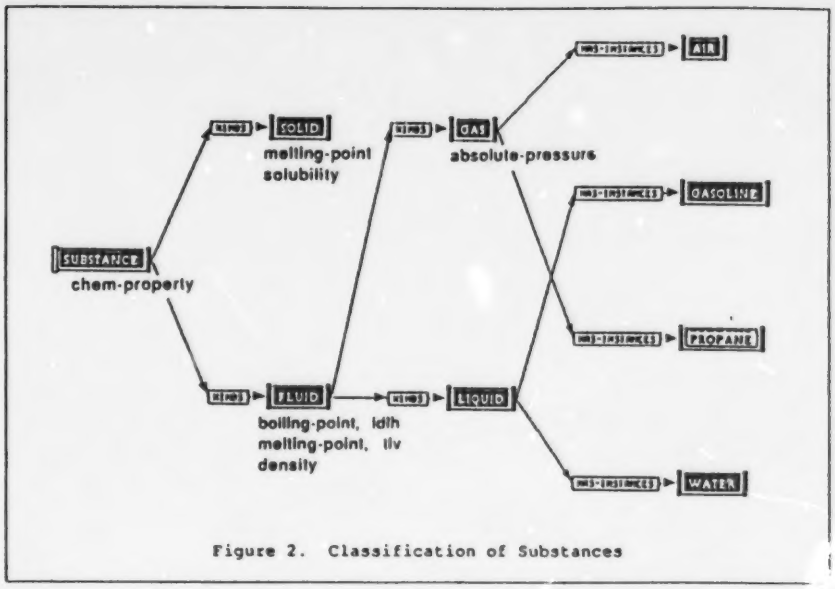

Figure 2. Classification of Substances

HERMES: The Expert System Approach

As with most tasks where human decision making capabilities are involved, that of forming timely and effective responses in a chemical spill situation is difficult to execute with the conventional approach of using mathematical or statistical models alone. However, there are features and characteristics of expert systems that suggest more natural ways for approaching the problems in emergency response management. The basic designs for the user interface, knowledge structures and functionalities of the HERMES prototype follow the emergency response process described above. There are features for entering case data, for representing both fundamental and heuristic knowledge, for making estimates of hazard levels and for generating countermeasure recommendations. These features are easily implemented with expert system concepts such as facts, frames, rules, daemons and inference mechanisms.

Facts

A fact is a collection of usually three items- for specifying an object-attribute-value triple. For example, the fact below describes the condition of an emergency situation by specifying INCIDENT as the object of interest, STATUS as an attribute for INCIDENT and UNSAFE as the value of STATUS.

< incident status unsafe >

Frames

A frame structure may be considered as a means for organizing all the facts about a single object. In HERMES, a frame called INCIDENT is used to represent all information associated with a spill situation, including all case data. An example set of attributes/slots and corresponding values for INCIDENT are given below (also shown in Figure 3).

```
substance:  anhydrous-ammonia
container-type:  tank
district-type:  unknown
activity-type:  unknown
fire-type:  low-intensity
leak-flow-rate:  100
leak-volume:  100
leak-source:  side
tank-damage-type:  dents
outlook:  sunny
temperature:  20
given-advice:
   "Remove all injured people from truck site."
   "Prevent further access to truck site."
.
.
.
```

Example facts that are generated from this frame are:

< incident substance anhydrous-ammonia >
< incident container-type tank >
< incident district-type unknown >

There are other functionalities typical of frame structures that HERMES takes advantage of. Meta-knowledge or "knowledge about knowledge" can be specified for each of the slots in a frame. These include facilities for specifying default values, allowable values and cardinality for a slot. Another feature, the daemon mechanism, is for specifying procedures that are automatically executed when a slot is modified. These features are important especially during implementation, relieving the programmer of much of the bookkeeping tasks.

The other frames in HERMES are for representing the different types of chemicals (propane, nitrogen, anhydrous ammonia), chemical properties (corrosive, explosive, cryogenic) and hazard levels (fire-potential-gauge, environment-danger-gauge, public-danger-gauge).

Frame Hierarchies

Frames also have a facility for specifying hierarchies and the accompanying inheritance behaviour. It is commonly used to establish a classification of objects and these objects are able to share slots and values. Linking concepts called is and instance allow connections between objects. A sample hierarchy is the taxonomy of chemical substances in Figure 2 (using corresponding ART inverse relations, KINDS and HAS-INSTANCES, for IS and INSTANCE). Because of the inheritance mechanism, the substance PROPANE will have the slots ABSOLUTE-PRESSURE, BOILING-POINT, .., CHEM-PROPERTY.

Rules

Rules are employed mainly for representing unexplained experiential knowledge-those backed by experience rather than theory. As such, it is usually difficult for the expert to articulate the decision rules he uses or how he brings knowledge to bear on the problem. For HERMES, the rules were acquired by

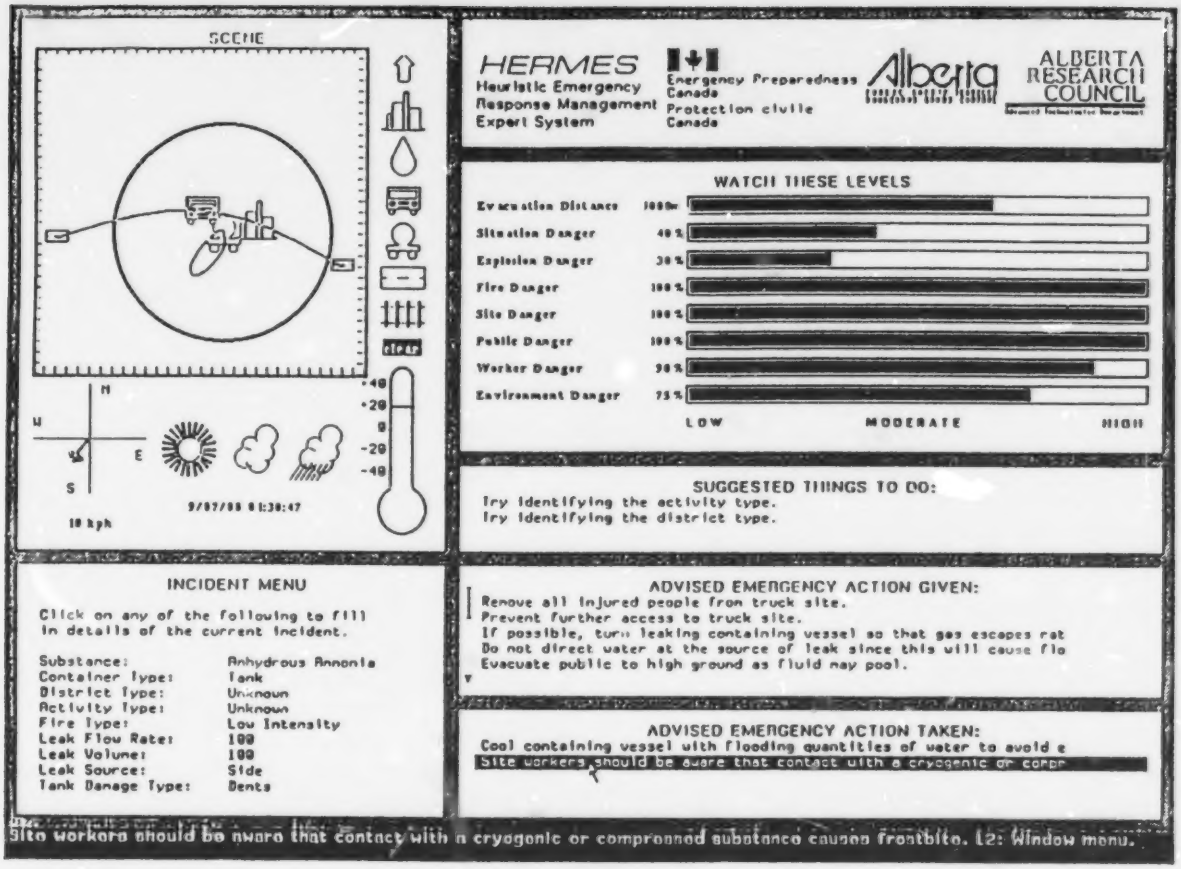
SCENE
HERMES
Heuristic Emergency
Response Management
Expert System
Emergency Preparedness Canada
Protection civile Canada
Alberta
ALBERTA RESEARCH COUNCIL
WATCH THESE LEVELS
Evacuation Distance
Situation Danger
Explosion Danger
Fire Danger
Site Danger
Public Danger
Worker Danger
Environment Danger
LOW
MODERATE
HIGH
SUGGESTED THINGS TO DO:
Try identifying the activity type.
Try identifying the district type.
INCIDENT MENU
Click on any of the following to fill in details of the current incident.
Substance: Anhydrous Ammonia
Container Type: Tank
District Type: Unknown
Activity Type: Unknown
Fire Type: Low Intensity
Leak Flow Rate: 100
Leak Volume: 100
Leak Source: Side
Tank Damage Type: Dents
ADVISED EMERGENCY ACTION GIVEN:
Remove all injured people from truck site.
Prevent further access to truck site.
If possible, turn leaking containing vessel so that gas escapes rat
Do not direct water at the source of leak since this will cause flo
Evacuate public to high ground as fluid may pool.
ADVISED EMERGENCY ACTION TAKEN:
Cool containing vessel with flooding quantities of water to avoid e
Site workers should be aware that contact with a cryogenic or compr
Site workers should be aware that contact with a cryogenic or compromised substance causes frostbite. F2: Window menu.

Figure 3. HERMES Interface

discussing different situations and how they are affected by specific input variable changes. The example rules below show some relationship between chemical properties and the evacuation distance.

```
IF
   substance is gas
   substance is not flammable or
      substance is not corrosive or
      substance is not poisonous
   fire type is low intensity or
      fire type is high intensity
THEN
   evacuation distance is 800


IF
   substance is liqui'
   substance is not flammable
   fire type is low intensity or
      fire type is impinging
THEN
   evacuation distance is 300
```

The if-part of a rule consists of conditions that must be satisfied for executing the rule while the then-part contains conclusions that are established in executing a rule.

Inferencing

The inference engine of an expert system is a mechanism for manipulating rules to form inferences and draw conclusions. All the facts, including those that are associated with frames, comprise the working memory of an expert system. Conditions of rules are matched against these working memory elements, resulting in more facts being established due to successful execution of then-parts of rules. This process continues until there are no more rules to fire. Just described is one type of inference mechanism called forward-chaining and is the one mainly used in HERMES.

Interfacing

Interfacing has become an integral part of any expert system. Interface routines are increasingly made to closely relate to the encoded knowledge. The HERMES interface is an excellent example of this practise. Frames are also used to define interfacing objects that will correspond to objects in the knowledge base. They are usually connected by daemons or software manipulation rules so that any modification on a knowledge base object is mirrored by an appropriate interfacing object.

Figure 3 shows the interfacing screen for HERMES. It simultaneously allows graphical input of case data in the SCENE window, textual input of case data in the INCIDENT MENU window and displays of output in the form of gauges for hazard assessment and menus for advice listings. With this interfacing scheme, the user is free to input any information when available and the output displays are immediately updated to reflect newly formed facts and conclusions.

Two HERMES Prototypes

The HERMES project currently consists of two prototype systems. The initial system was developed using Automated Reasoning Tool (ART) software on the Symbolics Lisp machine as a proof-of-concept. ART is a high-end AI development tool with sophisticated window and graphics systems, not to mention the extensive capabilities of the Symbolics Common Lisp programming environment, which facilitated prototyping. The system includes a tutorial mode that allows a trainee to acquire emergency response skills from the encoded expertise. The tutorial mode is conducted on a separate but similar interfacing screen [1]. HERMES-ART also incorporates an analytical model of gas dispersion into the atmosphere, a feature which assists response personnel in identifying evacuation and danger areas.

The second prototype runs on an 80286 or 80386 based computer and is written in the knowlege engineering shell GoldWorks and the graphics package Halo. It is an investigation into the performance of the HERMES approach in a smaller, portable and less expensive personal computer environment. Moreover, emergency vehicles are now being equipped with PCs for chemical database access and it would be desirable to have an expert system that can utilize the database. However, interface building facilities on the PC are less sophisticated, requiring more time for system development. Also, the resolution on the PC is much less and the screen shown in Figure 3 was reformatted on separate screens.

Conclusions and Future Work

The HERMES prototypes have proven successful in that they have demonstrated the capabilities and usefulness of the expert system approach in emergency response management. An informal comparison has shown that within the operating range of the system, HERMES is at least as good as a human expert in giving advice. And it is able to give advice quickly, without ovelooking variables that a human expert would miss in the same stressful situation. HERMES can act as an assistant to an expert by extending his capabilities, or as an expert advisor when an expert is not available. Finally, it has the potential to capture and distribute a wide range of expertise, creating a synergistic knowledge base and preserving experience.

As a prototype system, HERMES was extremely successful. However, to extend the prototype towards a usable product, several areas of further development are required.

More Substances

The prototypes handle only 10 substances while 3,000 would be required for a widely applicable system. To efficiently handle this many substances, the substance classification system will require more refinement, so that substances can be better represented according to their physical and chemical properties. Substances can then be grouped and inferences made to the properties in a class of substances and not to the substances themselves.

Environmental Modeling

While HERMES presently contains a model to calculate gas dispersion in air, models for soil and water dispersion have not been added to the system, even though these are well defined. Additionally, there is also the possibility of using the expert system to decide which of several models may be best suited to the given situation.

External Data Access

Because many models and decisions require precise data as input, it will be necessary to have access to large amounts of data. One example is that precise details of chemical properties, and related interactions between chemicals may need to be known. Another example is that a digitized map of a city sewer system could aid in suggesting evacuation requirements. Fortunately, in many cases large commercially available databases exist to supply such data. Therefore, it will be worthwhile to interface HERMES to these databases.

Uncertainty

The system does not presently have the ability to deal with uncertain facts and then propagate this uncertainty through to conclusions. If users were allowed to input the reliability of the input values, the system could not only indicate its confidence in any piece of advice given, but also decide between competing advice.

Temporal Reasoning

Some sense of time should be incorporated into the system which would allow, for instance, the deduction of the most effective way to schedule available time-dependent resources such as fire fighters. Such a system could also be useful for evacuation planning.

Different System Environments

While the existing system can run on certain non-portable or "office" computers, it may be desirable to have the system capable of running on a machine that can be taken directly to an emergency site. This could be a portable terminal connected to a main system through a modem and cellular telephone, or it could be a portable system unit.

Final Remarks

There are still many missing elements before HERMES can be fully operational. However, support for the project continues. Also, expert system techniques can be depended upon to facilitate the modification and evolution of the prototype into a complete production system.

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FATE AND BEHAVIOR OF TETRACHLOROETHYLENE SPILLED ON SOIL

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1.0 INTRODUCTION

Recent groundwater surveys in the United States have indicated that numerous drinking water supplies are contaminated with volatile organic compounds (VOCs), especially chlorinated hydrocarbons (Barbash and Roberts, 1986). One of the most common chlorinated hydrocarbons found in the aquifers is tetrachloroethylene (PCE), a popular solvent used in Canada and the United States. Eighty percent of the PCE is used in drycleaning and metal degreasing industries [Keil, 1978]. PCE has been included in the list of priority pollutants in the United States [U.S. EPA., 1979].

Tetrachloroethylene reaches the groundwater through releases into the soil environment through improper disposal practices, industrial impoundments, leaking storage tanks and accidental spills [Roberts et al., 1982]. Once released to the unsaturated soil, PCE migrates toward the groundwater. PCE's fate and behaviour during migration is influenced by various mechanisms, including volatilization, adsorption, desorption and degradation. Therefore, to properly predict how PCE behaves in unsaturated soil, these mechanisms must be understood.

Laboratory studies were conducted to investigate the fate and behaviour of PCE under various environmental conditions. These included batch studies to evaluate the kinetics for volatilization, adsorption and desorption of PCE from different soils. Also, soil column studies were conducted to monitor the migration of PCE in both dissolved and immiscible phases. Models have been developed which can predict the adsorption, leaching and penetration of dissolved PCE plume into the soil.

2.0 MATERIALS AND METHODS

Four types of media were selected for these studies. They included sandy loam soil commonly found in southeast Essex County in Southwestern Ontario, organic top soil purchased from a local nursery peat moss and granular activated carbon (GAC) purchased from Westvaco. The soils and peat moss were air dried and sieved to pass a 2.0 mm sieve. The GAC was used as received from the supplier. All four media were analyzed for the soil properties according to Black (1965), in the Methods of Soil Analysis and Table 1 shows the results of the analyses.

Both batch and column studies were conducted to evaluate the fate and behaviour of PCE in these media, The various procedures used in running the experiments are outlined in the following sections.

Table 1

Properties of the Media Used in this Study

Medium	pH	Chemical Organic Carbon (%)	Exchange Capacity (meq/100g)	Specific Surface Area (m /g)
Sandy Loam	6.4	1.0	14.2	22
Organic Soil	7.2	11.74	23.3	N.A.
Peat moss	3.5	49.42	Approx. 150	0.399
GAC	7.0	74.10	N.A.	1300

N.A. - not available

2.1 VOLATILIZATION OF PCE FROM SOIL

For volatilization of PCE from soil, sandy loam soil and organic top soil were used. The soils were weighed, 5.55 g of sandy loam soil and 3.3 g of organic top soil, and were placed in gas chromatograph (GC) vials. Three different sizes of GC vials were used to obtain area/volume values of 0.377, 0.77 and 1.43 1/m. Sufficient vials were prepared for each area/volume value to provide two samples every one-half hour for a total duration of four hours. The volume of PCE solution added to the vials were 1.0 mL and 1.6 mL for the sandy loam soil and organic top soil respectively. These volumes were added to bring the air dried soil to a field capacity moisture content. The aqueous solution added to the vials had a PCE concentration of 150 mg/L. Once the PCE solution was applied to the soil, the samples were capped at the appropriate time interval.

All vials were placed in a fume hood, which had a constant temperature and wind velocity. The temperature was maintained at 22 ^{o}C while the wind velocity was maintained at 10 km/h. Constant temperature and wind velocity are important as they affect the volatilization rate [Zytner et al., 1988b].

After capping all the vials, they were allowed to reach equilibrium at 30 ^{o}C [Zytner, 1988]. When equilibrium was reached, a gas sample from the headspace was withdrawn and analyzed for the PCE concentrations.

Volatilization from soil was also determined by applying pure PCE to the sandy loam and organic top soil. The soil was prepared as before and brought to the same moisture content by adding distilled - deionized water. Then 100 uL of pure PCE was applied to each vial. After that, the samples were then handled as described above for the aqueous PCE solution.

2.2 ADSORPTION/DESORPTION OF PCE BY THE DIFFERENT MEDIA

The adsorption characteristics were determined by weighing 5g of sandy loam soil, 5g of organic top soil and 0.4g of peat moss and placing them into 14 mL GC vials. However, only 50 mg of GAC was used because of its high adsorption capacity. The GAC was placed in 50 mL glass centrifuge tubes to increase the volume of PCE solution that could be used. Various concentrations of PCE, 22.5, 45.0, 67.5, 90.0 and 112.5 mg/L were added to the soil in the vials. The volumes of PCE solution added to each vial varied with the medium so that a minimum headspace was provided. The headspace was important as it not only affected the degree of mixing during shaking, but also controlled the mass of PCE lost through volatilization. Blanks containing only PCE solution allowed the measurement of volatilization losses.

The test vials were placed on a mechanical shaker for sufficient time to reach equilibrium, which ensures maximum adsorption. The equilibrium times used were 36h, 30h, 6h, and 20h respectively for sandy loam soil, organic top soil, peat moss and GAC [Zytner et al., 1989a]. After the adsorption equilibrium time was attained, the vials were removed from the shaker and centrifuged in a refrigerated centrifuge [Zytner, 1988]. The supernatant was removed and transfered into a 5 mL GC vial for analysis.

For the desorption isotherms, the medium was first subjected to adsorption as described above. The supernatant was then discarded and replaced with distilled - deionized water with no PCE. After that,the samples were treated in the same manner as for the adsorption study. The equilibrium times for desorption were 88hrs, 92hrs, 24hrs and 24 hrs for sandy loam soil, organic soil, peat moss and GAC respectively.

Finally an adsorption test was conducted to determine residual saturation concentrations. The residual saturation concentrations were determined by applying pure PCE directly to the air dried medium at the soils' respective field densities. The application of PCE continued until the sample reached field capacity and could no longer retain additional PCE. Experiments were repeated five times to obtain a representative value

2.3 COLUMN STUDIES

A schematic of the soil columns used in this study are shown in Figure 1. The columns were constructed of plexiglass tubes. A material which has been used successfully by reseachers to study the behaviour of organic chemicals in granular media [Salenieks and Henry, 1986 and Hoag and Marley, 1986]. The tubes had an inside diameter of 100 mm, a wall thickness of 5 mm and length of 1m. The ends of the tubes were threaded to provide leak proof seals when capped. The bottom cap was bevelled on the inside towards the middle to funnel the collected fluid to the center. A compression fitting was installed at the center to allow the samples to be withdrawn through a piece of tygon tubing. Silicon beads were applied to the interior of the columns at regular intervals to prevent channeling of the moisture between the soil and column wall.

Four columns of differnt depths were prepared for each soil to monitor the chemical front as it penetrated the soil. The soil core depths were 0.2, 0.4, 0.6 and 0.8 m respectively and the soils were placed at their respective bulk density. After the columns were packed, they were saturated with distilled-deionized water. Once the columns were completely saturated, they were allowed to drain to field capacity and the spill simulation was initiated. The quantity of PCE spilled, 10mL (16.22 g), was based on calculations using the adsorption isotherms with an equilibrium concentration of 150 mg/L [Zytner et al., 1988a]. This quantity ensured that the effluent from the longest columns would contain a significant concentration of PCE even after maximum adsorption had occurred.

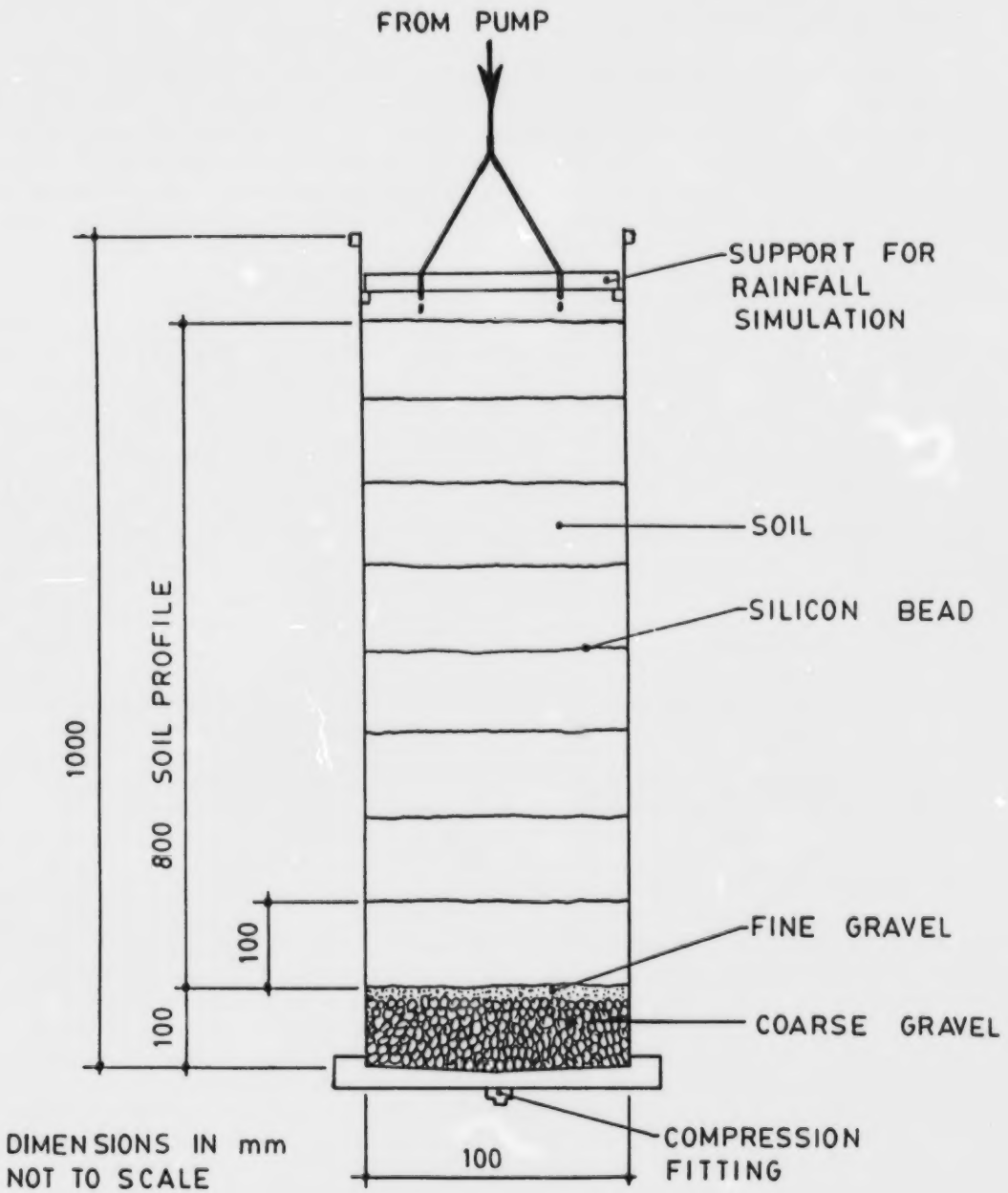

Figure 1. SOIL COLUMN

Distilled deionized water was applied by using a multi-channel autoclude pump at a rate of 76 mm/d (3 in/d). Two discharge tubes were placed above the soil surface of each column and were supported by a disk. This disk was rotated daily to prevent the development of flow channels in the soil column. Grab samples of the effluent were collected daily, except on Sundays, for the first 45 days of the operation. After the initial 45 days the sampling frequency was reduced to every second day. The samples were collected in a flask under vacuum, which was attached to the compression fitting installed in each column. The volume of samples drawn was 20 mL, which provided sufficient volume for the two subsamples, five mL each, that were required for the analysis. The sampling operation was completed in less then five minutes which ensured minimal losses of PCE through volatilization.

A second set of runs was conducted with chlorides as a tracer in the soil columns. These columns were prepared with fresh soil in an identical manner to the columns used in the PCE study. The movement of chlorides was used to determine the water velocity in both types of soils, because the chlorides do not react with the soil. The amount of chlorides spilled on the soil was 300 mg in dissolved 15 mL of distilled-deionized water (DDI). The concentrations of chloride were measured with an Orion Chloride Ion Electrode.

2.4 ANALYSIS OF PCE

The headspace technique was used to analyze the samples for PCE concentrations. [Dietz and Singley, 1979]. This analysis was performed on a Hewlett Packard Gas Chromatograph, Model 5890A, equipped with a methyl silicone gum capillary column [Zytner, 1988]. The temperature program was isothermal at 40 ^{o}C, with a retention time of 1.6 minutes. The results obtained for standard solutions injected were regressed linearly to obtain a calibration curve. Recovery was excellent with the correlation coefficient (r^2) in excess of 0.95.

3.0 RESULTS

Various types of experiments were conducted to determine the fate and behaviour of PCE present in differnt concentrations. The results obtained are presented in the following sections.

3.1 VOLATILIZATION OF PCE FROM SOIL

With the volatilization rate measured, the PCE concentration remaining after a specified time (t) can be calculated using Equation 1 [Zytner et al., 1988c]:

$$\frac{C}{C_o} = e^{-k_i t} \qquad (1)$$

Where

C = PCE concentration remaining in soil, mg/L

C_o = Initial PCE concentration in soil, mg/L

k_i = volatilization rate, 1/h

t = time, h

Equation 1 with the appropriate value for k_1, the volatilization rate, can be used to determine the PCE concentration remaining after a specified time t.

Therefore the data collected for the volatilization of PCE from soil were regressed using semi-log curve fitting [Zytner et al.,1988b]. The resulting volatilization rates are:

$$k_{SL} = 10^{(0.482(A/V)-1.002)} \quad (2)$$

$$kO_{RG} = 10^{((0.006Co-0.034)(A/V)-0.826)} \quad (3)$$

$$k_{PSL} = 10^{(0.210(A/V)-2.439)} \quad (4)$$

where

k_{SL} = volatilization rate for aqueous PCE from sandy loam soil, 1/h

k_{ORG} = volatilization rate for aqueous PCE from organic top soil, 1/h

k_{PSL} = volatilization rate for pure PCE from sandy loam soil. 1/h.

A/V = area to volume ratio,1/m

Co = starting PCE concentration, mg/L.

No volatilization rate was obtained for pure PCE from the organic top soil, because the volatilization rate was very low and no correlation could be obtained.

3.2 ADSORPTION/DESORPTION OF PCE

The adsorption/desorption data for the media were well represented by the Freundlich Isotherm equations obtained for each medium. The general form of each isotherm equation is:

$$\frac{X_i}{m} = K_i C^{1/n_i} \quad (5)$$

Where

X_i = mass of chemical adsorbed, or desorbed, ug

m = mass of soil, g

K_f = Freundlich ,Isotherms Constant K_f, for Adsorption and, K_{fd} for Desorption equilibrium constant,

C = equilibrium concentration, mg/L

$1/n_i$ = adsorption(desorption) intensity

Table 2 outlines the appropriate adsorption/desorption isotherms obtained for the various media tested.

Table 2

Adsorption and Desorption Isotherms for Dissolved PCE in Various Media

Media	Adorption	Desorption (deionized water)
Sandy Loam	$\frac{X}{m} = 5.193\ C^{0.657}$	$\frac{X}{m} = 2.51\ C^{1.009}$
Organic Top Soil	$\frac{X}{m} = 14.46\ C^{0.958}$	$\frac{X}{m} = 2.61\ C^{1.006}$
Peat Moss	$\frac{X}{m} = 264.0\ C^{0.861}$	$\frac{X}{m} = 40.20\ C^{1.01}$
Granular Activated Carbon	$\frac{X}{m} = 25280\ C^{0.557}$	$\frac{X}{m} = 1077\ C^{0.943}$

X/m = ug/g; C = mg/L

Table 3 lists the residual saturation concentrations determined for the four media. They have been reported on a mass per unit mass basis to allow comparison with the X/m values determined from the isotherms [Zytner et al., 1988c]

Table 3

Residual Saturation Concentrations of pure PCE in Various Granular Media

Medium	Residual Saturation Concentration (mg/g)
Sandy Loam	427
Organic Top Soil	771
Peat Moss	7763
Granular Activated Carbon	587

3.3 COLUMN STUDIES

The data obtained from different columns were analyzed using the column breakthrough theory [Reynolds, 1982]. The volume of throughput at breakthrough can be calculated from this theory. Breakthrough is defined as the volume of water passed through until the concentration is 0.05 of the initial concentration (C_O). By correlating these volumes with the different column lengths for the two soils, empirical equations were developed to calculate the

penetration depth. [Zytner et al., 1988d] Table 4 shows the penetrations depths as a function of throughput volume and time. The velocities of the dissolved fronts were calculated to be: 0.084 m/d for PCE in sandy loam soil, 0.026 m/d for PCE in organic top soil, 0.636 m/d for chlorides in sandy loam soil and 0.463 m/d for chlorides in organic top soil.

Table 4

Breakthrough Equations as a Function of Time and Volume for Columns at Field Capacity at an Application Rate of 650 mL/d (3in./d)

Type of Solute	Function of Volume	Function of Time
SLP	$Z_v = 133.3V_t$	$Z_t = 0.084t$
ORGP	$Z_v = 41.84V_t$	$Z_t = 0.026t$
SLCL	$Z_v = 1010V_t$	$Z_t = 0.636t$
ORGCL	$Z_v = 735.3V_t$	$Z_t = 0.463t$

SLP = designation for dissolved PCE in sandy loam soil
ORGP = designation for dissolved PCE in organic top soil
SLCL = designation for Cl^- in sandy loam soil
ORGCL = designation for Cl^- in organic top soil
V_t = volume of moisture added to spill, m^3
t = time, days
Z_v = penetration depth as a function of volume, m
Z_v = penetration depth as a function of time, m

The data collected to develop the empirical equations in Table 4 were also used to calibrate a contaminant transport model [Zytner et al., 1988d]. This model carries out a total mass balance for the four different phases: aqueous or dissolved phase, adsorbed phase, vapour phase and the pure or immiscible phase [Short 1985 and Palmer, 1987]. The model, which must be solved numerically on a computer, predicts the breakthrough time for a given soil profile. Breakthrough time is defined as the time that the concentration reaches 0.05 C_o at the end of the profile being simulated. Table 5 lists the breakthrough times calculated from the empirical equations and the contaminated transport model. Figure 2 is a typical plot of the breakthrough concentrations measured in the column and those concentrations predicted by the contaminated transport model for organic top soil.

4.0 DISCUSSION

The results presented have above been discussed in depth elsewhere [Zytner, 1988], In this paper emphasis is placed on the field application of the results.

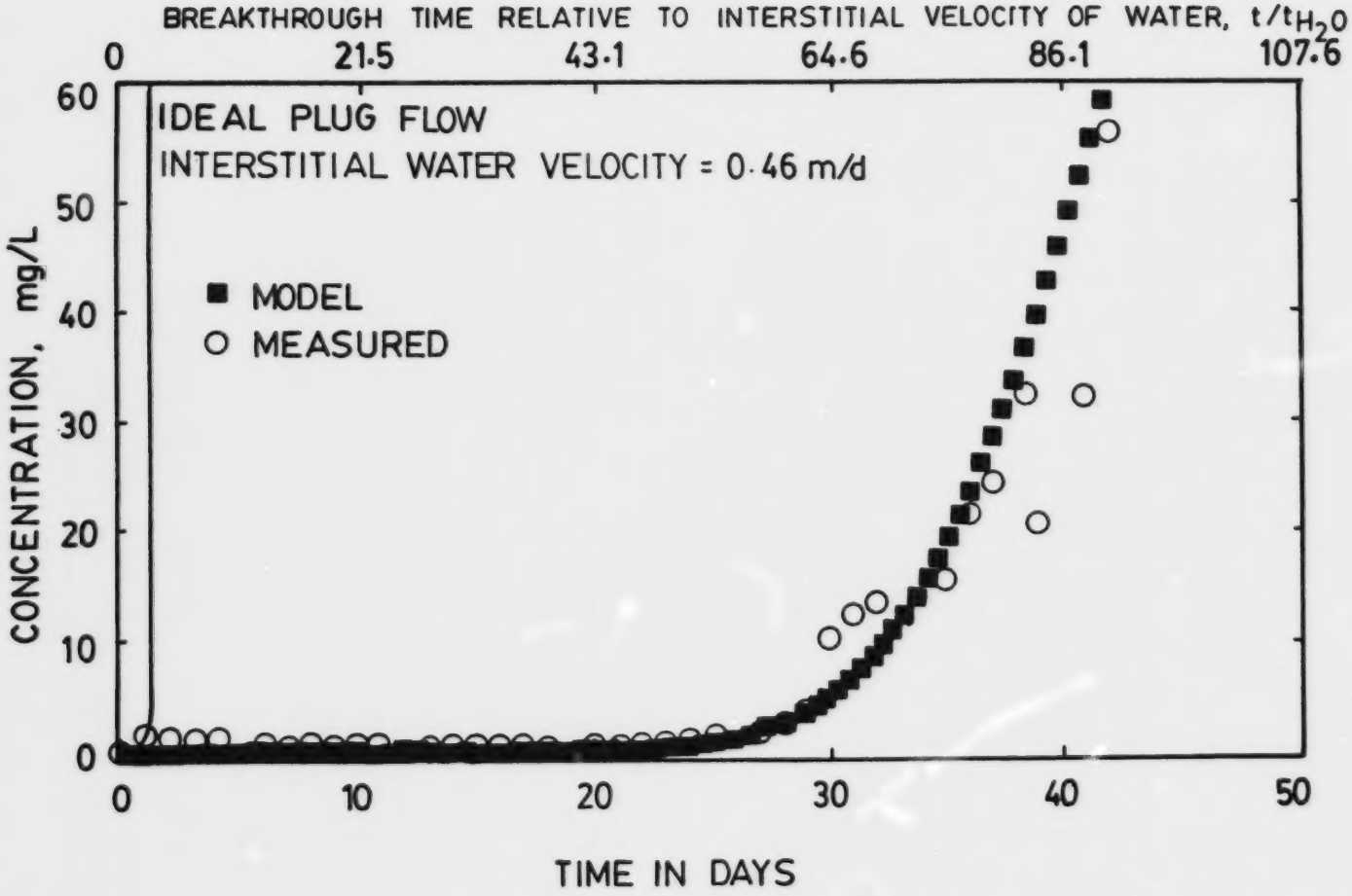

Figure 2. BREAKTHROUGH CONCENTRATIONS IN ORGANIC TOP SOIL FOR 0.8 METER LONG COLUMN

4.1 VOLATILIZATION OF PCE FROM SOIL

The model for the volatilization of PCE from the soil indicates that the volatilization rates are not only a function of the area to volume ratio but also depends on the concentration or mass of chemical present in the soil.

The experiments indicate that the volatilization of PCE from soil is rapid when the organic carbon content of the soil is low and the PCE is present in solution in the moisture contained in the soil [Zytner et al., 1988b]. However if the PCE is not in solution, as is the case for most spills, the volatilization rate is appreciably lower. In fact the volatilization experiment using pure PCE with organic top soil indicated no measurable volatilization rate.

Table 5

Breakthrough Times at Various Depths

Depth	Breakthough Time			
	Sandy Loam Soil		Organic Top Soil	
m	EB day	CTM day	EB day	CTM day
0.4	4.78	4.33	15.18	13.59
0.5	5.83	5.71	18.97	18.00
0.6	7.18	7.10	22.77	22.47
0.7	8.38	8.50	26.56	27.00
0.8	9.57	9.92	30.36	31.56

EB =breakthrough time calculated from the emperical breakthrough equations

CTM =breakthrough time predicted from the contaminant transport model

These observation suggest that different responses are possible when PCE is spilled on soil. If that the spill is confined to the upper soil layer, there exist a number of options for remediation. If the spill occurs on soil which has a high moisture content, the area of the spill can be isolated and the chemical can be allowed to volatilize into the atmosphere. However, if the soils' moisture content is low, and the soil has an organic carbon content comparable to the organic top soil, sufficient time will be available to excavate the soil.

4.2 ADSORPTION/DESORPTION OF PCE

The isotherm equations presented in Table 2 indicates that different media have different adsorption/desorption characteristics [Zytner et al., 1989a and Zytner et al., 1988c] These equations show that the best medium for adsorbing dissolved PCE is granular activated carbon. Therefore in situations where dissolved PCE must be retained and prevented from migrating, medium like granular activated carbon or peat moss should be used.

In order to determine the mobility of PCE in soils, the Freundlich adsorption equilibrium coefficients can be divided by the organic carbon content,to obtain the soil-water partition coefficient (K_{OC}) [Roy and Griffin, 1985]. When K_{OC} is less then 100, the chemical is considered highly mobile, whereas when it exceeds 1000 the chemical is considered immobile.

media tested in this study, an average K_{OC} of 330 was obtained. Thus, it can be stated that PCE has medium mobility in soil. This is consistent with what was reported in the literature for PCE [La Poe, 1985, Schwarzenbach and Westall, 1981 and Roy and Griffen, 1985]

When a chemical spill occurs, the chemical is most likely be in its pure form. From the residual saturation values given in Table 3, peat moss appears to be an ideal medium to contain the spill. The peat moss is ideal as it can adsorb up to eight times its body mass. An additional benefit in using peat moss is that it is a relatively inexpensive natural medium.

4.3 COLUMN STUDIES

The data on column studies shows that the dissolved PCE front volocity was retarded through interaction with the soil. Based on the dissolved front velocities, it appears that the velocity in organic top soil is approximately one-third of the velocity in sandy loam soil. Thus, if a spill occurs, one would have more time to respond before the chemical reaches the groundwater with the organic top soil, when it is compared to the sandy loam soil. However, it should be noted that even in the sandy loam soil, the dissolved PCE front velocity was retarded as compared to the chloride tracer velocity.

The data collected for the column studies have shown that the residual saturation of soil is important [Zytner et al., 1988d]. Initially, soils with a high residual saturation, such as organic top soil, adsorb PCE in the upper layers. Thus, if excavation is carried out before it rains, the majority of the PCE can be recovered before it migrates to the groundwater. However, if rainfall begins before the soil is removed, the chemical will slowly dissolve and be transported into the groundwater.

The empirical equations in Table 4 and the calibrated transport model are extremely beneficial for calculating the depth of penetration. A residual excavation plan can be developed after determining how deep the dissolved chemical has penetrated into the soil. This ensures that no PCE remains in the soil.

4.4 LEACHATE STUDIES

Futher analysis of the data has led to the development of a model that can predict the adsorption of PCE on a given soil and successive leaching of PCE from contaminated soil using water [Zytner et al., 1989b]. This model can be used to develop a set of nomographs for a given type of soil. Figure 3 shows a typical nomograph for organic top soil. In Figure 3, XA is the total mass of PCE adsorbed by the soil, X_{des} is the total mass of PCE desorbed from the soil, V_{des} is the volume of water added to the soil and M is in the mass of soil. This nomograph can be used to predict the volume of water required to leach all the adsorbed PCE from the soil.

5.0 CONCLUSIONS

Laboratory studies on the fate and behaviour of tetrachloroethylene in soils have shown that:

- PCE spilled on soil having a high moisture content will volatilize rapidly. Best solution is to cordon the area and allow PCE to dissipate naturally into the atmosphere.
- PCE spilled on soil that has a low moisture content and high organic carbon content will volatilize slowly. Sufficient time should be available to excavate and dispose of the soil.

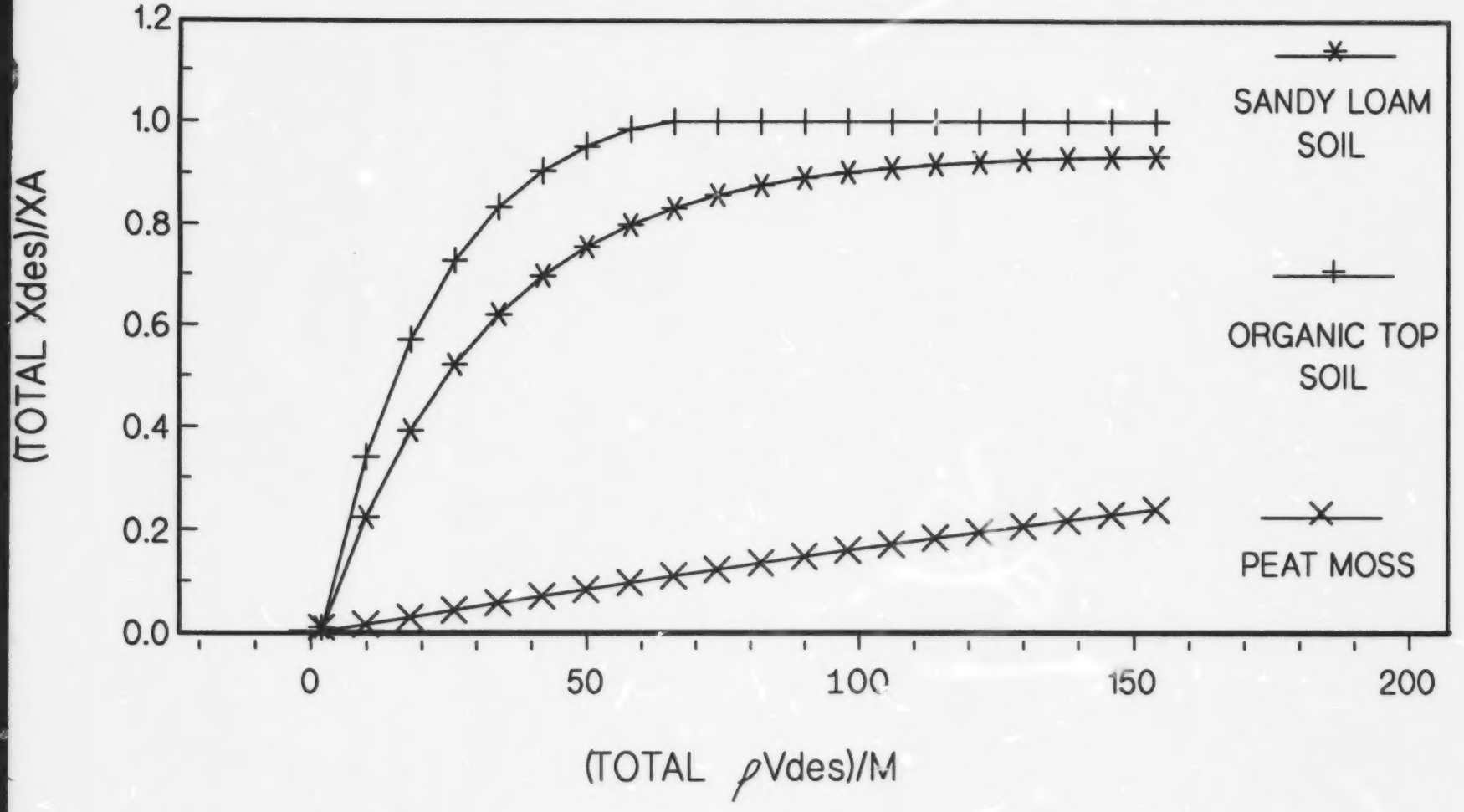

Figure 3. (TOTAL X_{des})/XA vs (TOTAL ρV_{des})/M FOR VARIOUS TYPES OF SOIL

- Media with high organic carbon content, such as granular activated carbon and peat moss, are ideal for adsorbing and retaining dissolved PCE.
- Peat moss is an ideal medium to adsorb and retain pure PCE because it has the capacity to adsorb eight times its body mass.
- The penetration depth and breakthrough times of PCE in organic top soil and sandy loam can be predicted by using the empirical equations given in this paper.
- A calibrated model has been developed to predict the unsaturated flow of PCE in soil. The model indicated that the organic content in soil retards the migration of PCE under spill conditions.
- A nomograph has been developed to predict the leaching of PCE from contaminated organic top soil. The nomograph can be used to predict the quantity of water required to successively leach the adsorbed PCE. Similar nomographs can be developed for other soils.

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HEAVY GAS DISPERSION IN TERRAIN WITH OBSTACLES

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ABSTRACT

Scale model testing was conducted in the RWDI boundary layer wind tunnel to determine the impact of arrays of obstacles on the path of a heavy gas cloud. The parameters of interest included terrain roughness, flow path, arrival time, dilution rate, and concentration fluctuations. Cloud arrival times were first determined from flow visualizations of the cloud translation, and later supplemented with concentration fluctuations measured with a high frequency Flame Ionization Detector. The obstacle arrays consisted of cube blocks arranged on a rectangular grid with uniform spacing. Flow visualization of the cloud passage during calm conditions showed that immediately after a release with uniformly-spaced obstacles, a circular cloud formation was observed, while at later times the cloud tended toward a surprisingly exact diamond shape. As the wind speed was increased, the diamond shape became less distinguishable. The observed concentration profiles showed an increased dose-time relation with obstacles present. The concept of a threshold wind speed was identified, above which cloud behaviour was not greatly affected by the presence of the obstacles.

1. INTRODUCTION

This paper describes the first part of a Research and Development Project performed by Rowan Williams Davies & Irwin Inc. (RWDI) for the Ontario Ministry of the Environment (MOE). The ultimate goal of the Project is to develop a computer model which provides the capability of predicting the behaviour of a heavier-than-air gas cloud during a spill in an urban area. Current mathematical models apply to smooth terrain only. This is a significant limitation because accidental spills are likely to have the most impact in suburban or urban settings. The novel feature of the model will be the ability of this model to account for the presence of obstacles in the path of the gas cloud and for certain types of non-uniform terrain. Toward this end, several heavy gas experiments were performed at model scale in the RWDI wind tunnel at the Guelph facility. The setup, wind tunnel calibration, instrument calibration, testing of uniform arrays and data analysis comprised Phase I. The testing of non-uniform arrays and detailed model development will comprise Phase II. We report in this paper on Phase I.

2. PHYSICAL MODELLING OF DENSE GAS RELEASES

Physical modelling consists of reproducing the important physical phenomena at full scale on a much smaller model. The motivation is derived mainly from

the ability to predict problems which might occur at full scale on a smaller, less costly scale model. Accurately representing the physical phenomena consists of holding certain parameters constant at both full and model scale. In theory for the case of atmospheric modelling, a wind tunnel simulation of heavy gas dispersion is representative of a field trial if similarity is ensured for the following parameters:

i) Reynolds number of the flow, $Re = D\ U\ \rho/\mu$
ii) Bulk Richardson number, $Ri = g\ L\ [\ (\ \rho_g - \rho_a)/\rho_a\ ]\ /\ U^2$
iii) Release density ratio, ρ_g/ρ_a
iv) volume flux ratio, Q/L^2U;
v) wind velocity profile, U vs z;
vi) surface roughness, z_o/L;
vii) turbulence intensity; and
viii) ratio of length scale of turbulence at full to model scale.

Not all of these criteria can be satisfied in practice. The Reynolds criteria cannot be satisfied for models of 1:100 to 1:600 scale because the model wind velocity required by the bulk Richardson number similarity becomes very low, and it is difficult to obtain a good simulation of the boundary layer at low speeds in the wind tunnel. Fortunately, a reasonably complete simulation can be obtained, even in violation of Reynolds similitude[1].

The bulk Richardson number represents a ratio of gravitational and inertial forces. All investigators agree the bulk Richardson number (or Froude number and density ratio) must be equal at full and model scale. Often the density ratio is increased during model testing to allow a corresponding increase in the model wind velocity. In a practical sense, a higher velocity simulation is much easier to perform. Ideally the volume of release is scaled by a characteristic dimension and time scale. The radius or height of the release is often used as the appropriate length scale. If Richardson Number (modified Froude number) similarity is maintained, then time scales are obtained from:

$$t_o = r_o / U_o \qquad (1)$$

and

$$(r_o / U_o)_{\text{model}} = (r_o / U_o)_{\text{full scale}} \qquad (2)$$

where

$$U_o = [\ g\ h_o\ (\ \rho_g - \rho_a\ )\ /\ \rho_a\ ]^{1/2} \qquad (3)$$

and r_o, h_o are the initial radius and height of the release respectively. Equations 1, 2 and 3 can be used to relate the model time scale to full scale, which is important when comparing data between the two.

The wind mean velocity profile over the model should have a shape which is similar to the full scale wind profile. The absolute values of the scaled velocities are obtained from Richardson similitude.

The surface roughness is scaled by dimension. Here, the parameter z_o/L is kept constant. The turbulence intensity of the wind in the along wind direction should be similar at both scales. The length scale of turbulence should be correct in relation to the model scale. Later we shall see that for a partial boundary layer simulation, some of these criteria may not be satisfied exactly. In these tests, the wind tunnel simulation is that of a boundary layer with neutral thermal

stability.

The first task in wind tunnel modelling is to set the model scale. The main constraint is to keep the Richardson number, Ri, the same at both full and model scale. Preferably, the velocity measured at the top of the boundary layer in the wind tunnel should be maintained above 2 m/s since control and measurement of the wind speed are more difficult below this value.

Data from the full scale velocity profile[2] (see below) were found to fit a power law profile with an exponent of 0.11 in the lower part of the boundary layer. From this profile, a comparison of different scales suggested that simulations might be performed at 1:50 and/or 1:100 model scales. At model scales less than 1:100 (i.e. 1:300 or 1:500), a reference velocity much less than 2 m/s is required. An increase in gas density allows an increase in the wind speed (while keeping Ri constant) but the criterion is best satisfied at 1:50 and 1:100 scales. Simulations were thus performed at the 1:50 and 1:100 model scales.

After some consideration, it was decided to conduct instantaneous releases similar to the full scale field trials carried out at Thorney Island on the southern coast of England during the early 1980's. The details of several of the tests performed as part of the Phase I Heavy Gas Dispersion Trials (HGDT) may be found in McQuaid[2,3].

For design purposes, Trial #13 was selected for simulation because of the relatively high wind speed. It was thought that this trial might be easier to simulate in light of the difficulties with low wind speed operation.

The upwind fetch of the RWDI wind tunnel was adjusted to create the velocity profile shown in Figure 1. The curve shown in this figure is the power law - velocity α (height)$^{0.11}$ which was found to fit the lower part of the boundary layer well. A better fit over the entire boundary layer may be obtained with a somewhat higher value of the exponent. However, it is the lower region that is important for heavy gas dispersion.

The longitudinal turbulence intensity variation with height as measured in the wind tunnel is plotted in Figure 2. The reference height in the wind tunnel was 1.5 m or 150 m at full scale for 1:100 ratio. At the 10 m (full scale) height, the turbulence intensity is about 2% higher in the model than at full scale. This indicates a reasonable agreement with the full scale value[3] of 13.4%. The impact on simulation is a possible higher level of mixing in the model compared with full scale.

The turbulence spectra were measured at three different heights. From the spectra the length scale of turbulence in the modelled boundary layer was found to be more representative of a 1:200 scale than the intended 1:100 scale boundary layer. This means the larger eddies are not present and the modelled length scale is thus smaller because of their absence. Since the near-field is of concern here, the absence of the larger eddies is not expected to produce significantly different results with respect to the dispersion process.

3. EXPERIMENTAL PROCEDURE

Design of the Release Canister

The wind tunnel simulation of the instantaneous releases of heavy gas required an appropriate design for the holding tank and release mechanism. Since the full scale release consisted of a cylindrical tent 13 m high by 14 m wide, a

cylinder was chosen for model scale. Both 1:50 and 1:100 release canisters were constructed as shown in Figure 3. The actual dimensions of the model release canisters are given in Table 1.

The aspect ratio (height to diameter ratio) was kept close to unity within the constraint of using readily available materials. Two struts supported the cover of the cylinder. A thin layer of foam was glued to the underside of the cover to seal the top. When activated, two solenoid valves allowed the cylinder to fall away from the top cover and through the floor of the tunnel. Leakage on the underside was prevented by the installation of rubber seals which were slightly compressed when the canister was locked in place in preparation for filling. The release design proved to work very well.

TABLE 1. RELEASE CANISTER DIMENSIONS

SCALE RELEASE	1:50	1:100
Height, H (cm)	27.56	12.6
Diameter, D (cm)	25.08	14.2
Volume (cm^3)	13,630	2001
Aspect Ratio, H/D	1.10	0.89

Flow Visualization

Flow visualization studies were performed to obtain a detailed visual record of the impact of obstacles on the flow path of the cloud. Two sets of flow visualization data were obtained. The first set were taken in a test configuration located outside the wind tunnel. Hence, these data were taken in a calm or still-air condition. Releases were carried out over smooth flat terrain and then on the same flat terrain but with obstacles. Two different obstacle configurations were studied, termed half-coverage and full-coverage. These are illustrated in Figure 4.

A second set of flow visualizations were taken in the wind tunnel. The set up is shown in Figure 5. The obstacle arrangements were similar to the first set except that only the half-coverage configuration was tested. The obstacle coverage downwind of the release extended twice as far as the coverage used in the calm wind tests. Releases were performed at model scale windspeeds of 0, 1 and 2 m/s (measured at 10 m height, e.g. 0.1 m at 1:100 scale) over smooth flat terrain as well as over obstacles located on flat terrain. Both 1:100 and 1:50 scale releases were studied.

The released gas was a mixture of air and Freon 12, with mineral oil mist added to mark the cloud. The density of the release was measured to be 3.9 kg/m^3 or 3.2 times the weight of air. Cameras were mounted directly overhead and to the side of the release canister. This provided both birds-eye and profile views of the gas cloud dispersion.

Concentration Measurements

Based on a review of the literature, the measurement of gas concentration was initially to be performed with aspirating hot film probes, as this method was used by several researchers in the field. We purchased three probes and found that

accurate measurement of gas concentration was impossible, without extensive modification to these "off-the-shelf" probes. The problems consisted of low signal response, volumetric sample flow was too high, probe etching occurred if Freon was used, and high pressure and temperature sensitivities. Because of time constraints, an alternate method was sought. The search resulted in the purchase of a high-frequency Flame Ionization Detector built in the U.K. by Cambustion Ltd. The fast response FID was developed for high speed sampling of combustion engines, specifically the diesel engine. Recently, the instrument has found application in gas dispersion research.

The overall principle of the FID operation may be described in a simple manner although the process is very complex. A sample of air containing a hydrocarbon as a tracer (say propane at 0.01% by volume) is drawn into the sample head where it is burned in a hydrogen (H_2) flame. The burned hydrocarbon produces ions in proportion to the amount of hydrocarbon initially present. This process is called chemionization. The movement of the ions to an electrode sets up a current that is proportional to the initial concentration of the hydrocarbon. As the concentration of propane increases in the sample flow, the ion current becomes correspondingly larger. Thus, a measure of the concentration may be obtained by suitable calibration techniques, i.e. using samples of different gas concentrations which are traceable to standards. The high response feature is derived from the combination of the sample flow and fuel mixture in a sample head located close to the source and away from the unit proper. The response depends on the sample flow, the length of the sample tube, fuel mixture and flow, sample tube diameter and sensitivity of the unit to the particular hydrocarbon being measured. Depending primarily on sample tube length and sample flow rate, a response of up to 350 Hz is possible.

A sample flow analysis was conducted using a computer code called "satflap" supplied by Cambustion Ltd. to estimate design data (length and diameter) for the sample tube. Since it was necessary to sample near obstacles, a 217 mm length was selected as the appropriate sample tube length. The tube I.D. was 0.010" or 0.25 mm; the O.D. was 0.020" or 0.50 mm. For a sample flow of 37 cc/min, the frequency response is well over 100 Hz.

Calibrations of the two FID channels are plotted in Figure 6. All calibrations were performed at the following operational flow rates: 300 cc/min air, 50 cc/min hydrogen, 18 cc/min sample flow under 200 mm Hg vacuum. These operating conditions were maintained and held constant for all subsequent testing. In the graph, concentrations of % (by volume) propane in air are plotted against the voltage output for the particular instrument range. A linear regression model was used for data prediction in each case. The error in the model prediction was sometimes greater than 10% especially at concentrations less than 10 ppmv, but overall the fit was generally good.

The frequency response of each unit was measured by rapidly passing a jet of gas with known concentration, past the end of the sample tube and plotting the response against time. With a sample flow of 18 cc/min, the time constant was measured to be less than 5 msec, and with a sampling rate of over 300 Hz the frequency response of the system was measured to be about 50 Hz.

The gas mixture used in the releases to be monitored with the FID was made heavy by adding sulphur hexafluoride, SF_6. The measured density was 3.9 kg/m^3

as in the flow visualization tests. The SF_6 actually decreased the sensitivity of the probe, probably the result of the combustion of SF_6 in the H_2 flame. Because of this, a calibration correction factor was developed to correct the measured values of concentration for the effects of SF_6 in the gas mixture. This correction factor was observed to be most significant above 20% SF_6.

4. TEST RESULTS - FLOW VISUALIZATION

Photo Study

Overhead photos of selected spills at 1:50 scale are shown in Figures 7 through 12. A release in calm wind with no obstacles present (Figure 7) shows a very uniformly spreading circular cloud. Also evident, especially at later times, is a rolling cloud front. By comparison, an identical release into a uniform array of obstacles (Figure 8) shows a striking difference. Here, a diamond-shaped cloud develops. The frontal flow along the open corridors appears to move faster than flow away from the corridors, which gives rise to the characteristic diamond shape. Other cloud shapes were created by varying the block spacing (not shown here), but varying the block size did not have a significant effect. Also, the cloud arrival time to a specific location away from the release is influenced by the presence of the obstacles; the cloud front advances faster in the corridor compared with the smooth terrain release; the reverse is true for a cloud travelling in the directions at an angle to the corridor.

Releases identical to those above were done at full scale wind speeds of 5 and 10 m/s. These are illustrated in Figures 9, 10, 11 and 12, respectively. Under low wind conditions with smooth terrain, the cloud slowly translates downwind while maintaining an almost circular shape. The presence of obstacles under low wind conditions, tends to impact the cloud in a manner similar to the calm wind case, i.e. the diamond front is distinguishable although the delineation is not as clearly defined as in the calm wind case. Under high wind conditions with no obstacles, the dispersion event is significantly shortened. The wind shears, pushes and disperses the cloud downwind of the release. Lateral spreading is somewhat reduced. The presence of obstacles under high wind conditions does not seem to affect the cloud dispersion to the same extent as in low wind. There appears to be some threshold wind speed which, when exceeded, washes out the cloud shapes experienced at lower speeds.

Modelling

By reducing the videotape record to a series of photographs, the horizontal dimensions of the cloud could be determined and a time/distance history of the cloud front under a variety of release conditions ascertained. For the 1:50 release, the cloud front distance as a function of elapsed time is shown in Figures 13 and 14 for a variety of block size and coverage configurations. Figure 13 shows the distance measured along the corridor and Figure 14 shows the distance as measured at a 45° angle from the corridor, where the gas must follow a tortuous path around the blocks. Since the near field is of interest, the initial spreading phase has been modelled. The release is considered as a cylindrical cloud of known dimensions. Using a simple box model approach to heavy gas dispersion, the gas slumping phase is taken to be controlled by gravitational effects. Assuming a constant cloud volume during this phase gives the following

relationship for the rate of spread of the cloud under still air conditions:

$$r^2 = r_o^2 + 2\,C\,t\,[\,\{\,(\,\rho_g - \rho_a\,)\,/\,\rho_a\,\}\,g\,V_o\,/\,\pi\,]^{1/2} \qquad (4)$$

where r is the cloud radius at time t, r_o is the initial cloud radius at t=0, C is a constant, ρ_g and ρ_a are the gas and air densities respectively, V_o is the initial gas volume, and g is the gravitational constant. In theory[4], the constant C could be either 1 or 1.414, but experimental results have shown C=1 to be the better choice[5,6]. In order to improve the model fit, the constant C was determined empirically through (4) for each time segment. The resulting values were then averaged. With no obstacles, the average value of C was found to be 1.19. When this value for C is used in (4), the lower curve on Figure 13 results. The upper set of points in Figure 13 stem from data using a smaller obstacle (3.5 cm by 3.5 cm). The C value was calculated to be 1.75 as indicated on the upper curve in Figure 13. The value of C, averaged over all configurations, was found to be 1.54.

In order to account for the slowing of the cloud front away from the corridor, the geometry of the cloud shape was used to develop an extension to the simple model. A geometric factor f(t) was empirically determined to be:

$$f(t) = [\sin 45/\sin(135-\alpha)][e^{-\beta t}\{\sin(135-\alpha)/\sin 45\} + (1-e^{-\beta t})] \qquad (5)$$

where α is the angle (in degrees) of the radius from the horizontal axis and β = 1 with obstacles and β = 0 without. Note that for β = 0, f(t) = 1 which gives the equation of a circular cloud front. With β = 1, as $t \rightarrow \infty$, equation (5) reduces to $\sin(45)/\sin(135 - \alpha)$. The geometric factor f(t) is then multiplied by the radial distance from equation (4) to give r_d, the distance of the cloud front from the release:

$$r_d = r\,f(t) \qquad (6)$$

where r is the distance calculated by (4), and f(t) is the shape factor as a function of time t. This model is plotted in Figure 14 for the 1:50 scale release. The agreement is reasonably good with obstacles present.

Work is currently in progress on developing a more comprehensive numerical model of the cloud dispersion in obstacles to improve on the above simple expression.

5. TEST RESULTS - CONCENTRATION FLUCTUATIONS

Model data are compared with Thorney Island Trial #13 in Figure 15. The ratio of measured downwind concentration to initial concentration in the release canister is plotted against the dimensionless time t^* (= t/t_o), where t_o is given in equations 1 and 3. Note, although the match between full and model scale parameters was not exact, the modelled concentration profile and peaks generally agree with full scale values, well within a factor of two. The cloud arrival time was somewhat longer in the model case, the difference between 20 and 30%. This is likely because of the difference in sensor heights. The inexact Ri scaling may also contribute to time of arrival differences between model and full scale.

The influence of obstacles on the cloud concentration is demonstrated by comparing Figures 16 and 17. Test conditions were identical except for the presence of the obstacles, and the sensor was positioned in the corridor 55 m downwind. At all windspeeds, the integrated area under the curves is larger with the obstacles in place. Also the peaks are similar in magnitude for all but the calm wind case. Thus, the dose-time relation has been increased with obstacles in place. In other words, the cloud hangs around longer. It also seems the concept of a threshold wind speed is further supported by this data. Above a particular speed, the profiles are similar, but below that speed the profiles are significantly different. This can be seen by comparing the 5 m/s data and the 10 m/s data.

7. CONCLUSIONS

The influence of obstacles on instantaneous releases of heavy gas has been studied by physical modelling. Flow visualization records and concentration profiles were presented which identified the concept of a threshold wind speed. Above this speed, the cloud behaviour was not significantly influenced by the obstacles. However, below this speed, the dose-time relationship was significantly increased. Additional research is needed to further define the dependence of this threshold on both wind speed and local terrain.

8. ACKNOWLEDGEMENT

The authors acknowledge the support of the Ontario Ministry of the Environment in this work.

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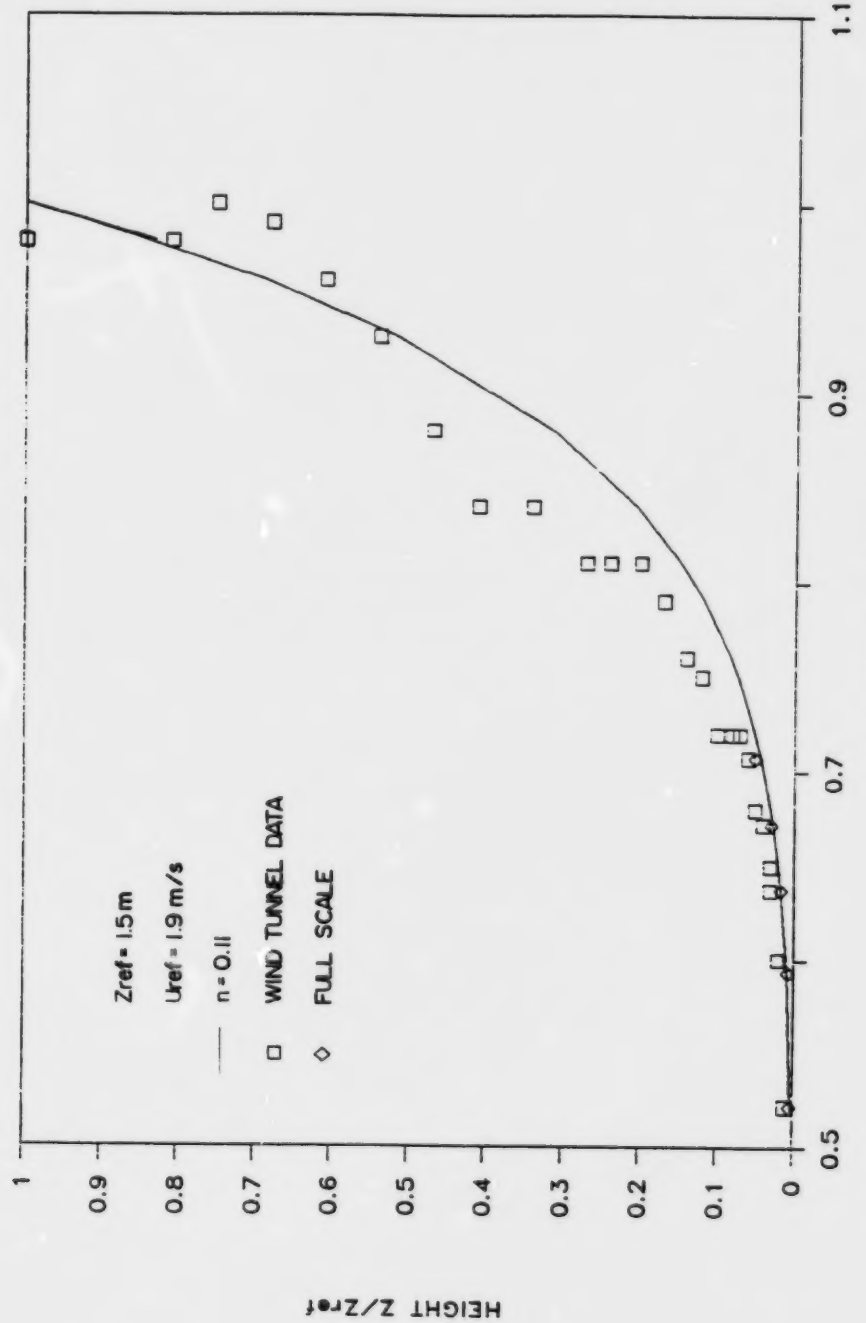

Figure 1. Mean velocity profile

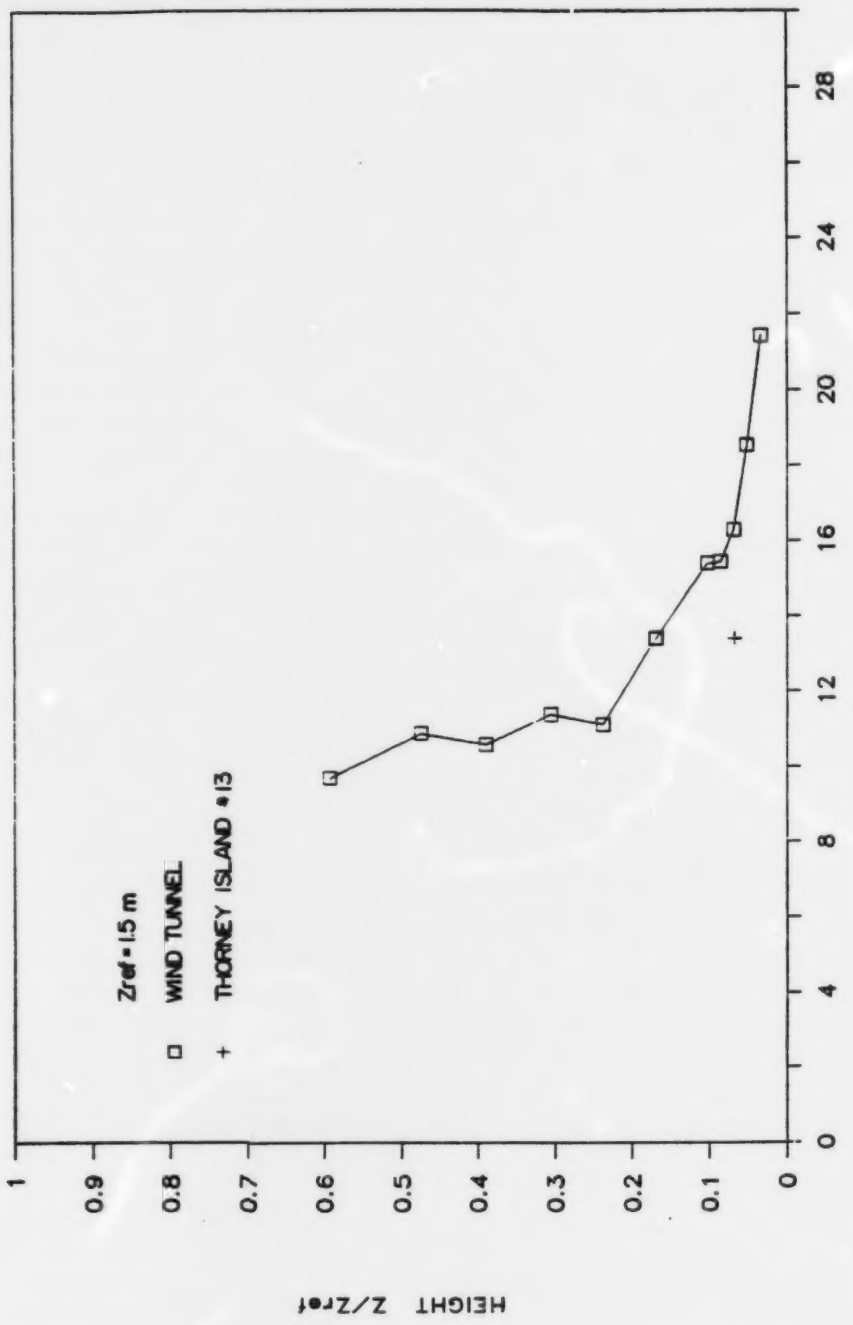

Figure 2. Turbulence profile approaching model

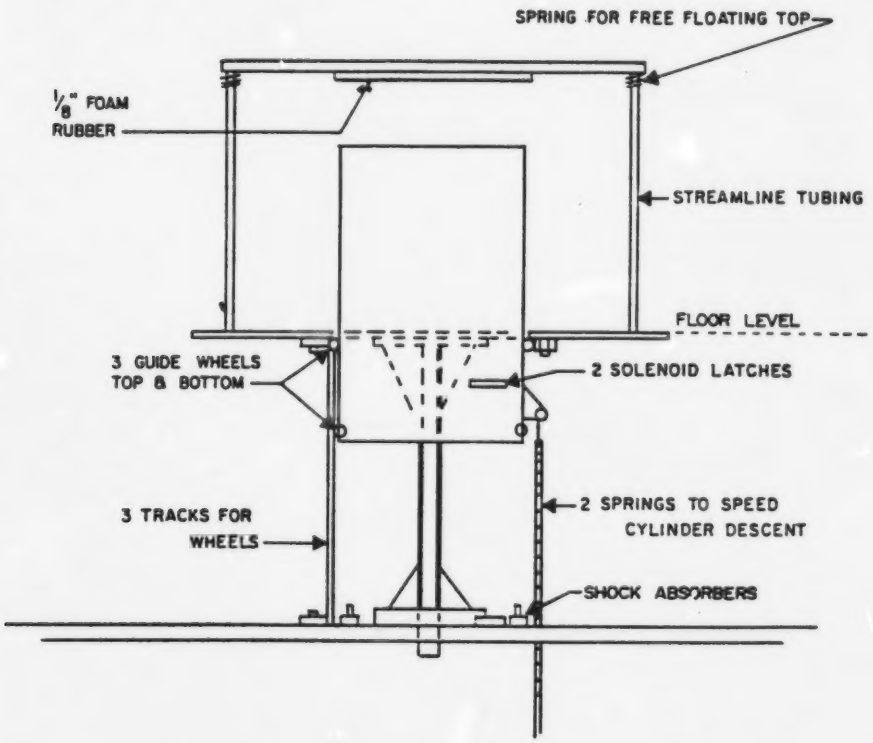

Figure 3. Release canister

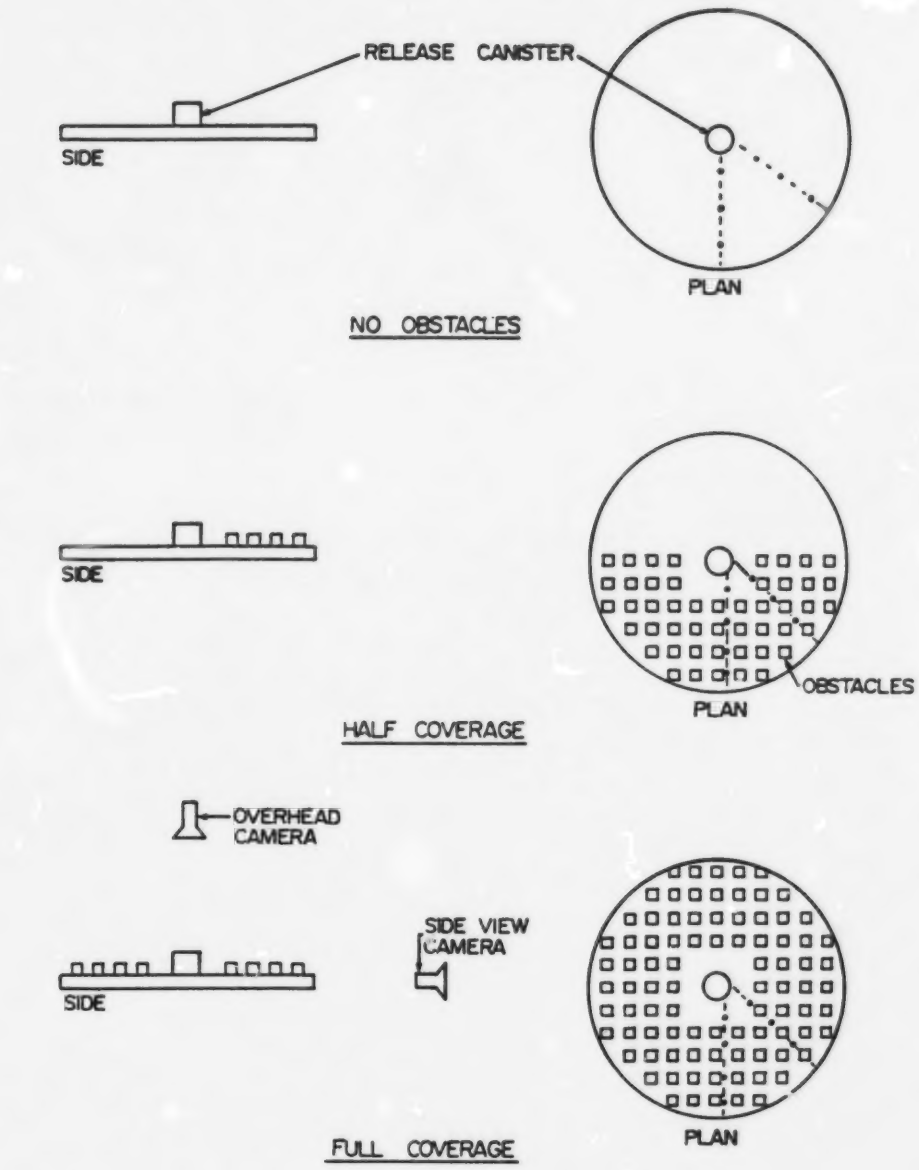

Figure 4. Schematic for still-air tests

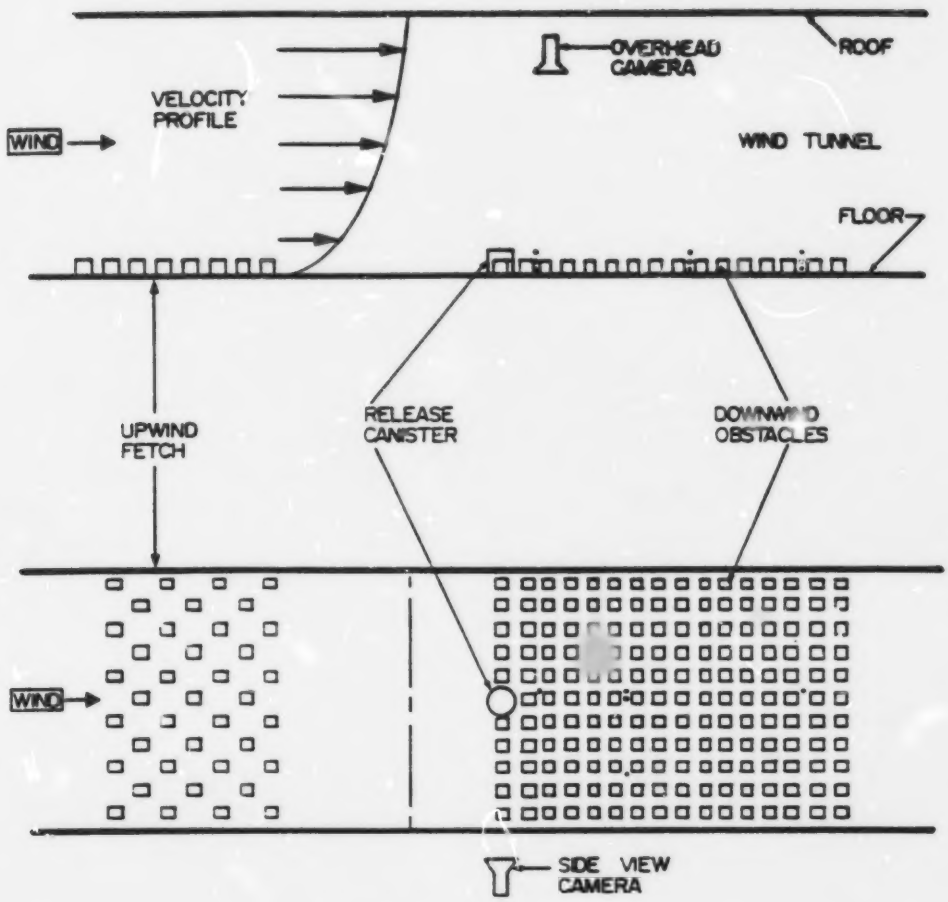

Figure 5. Schematic of tests in wind tunnel

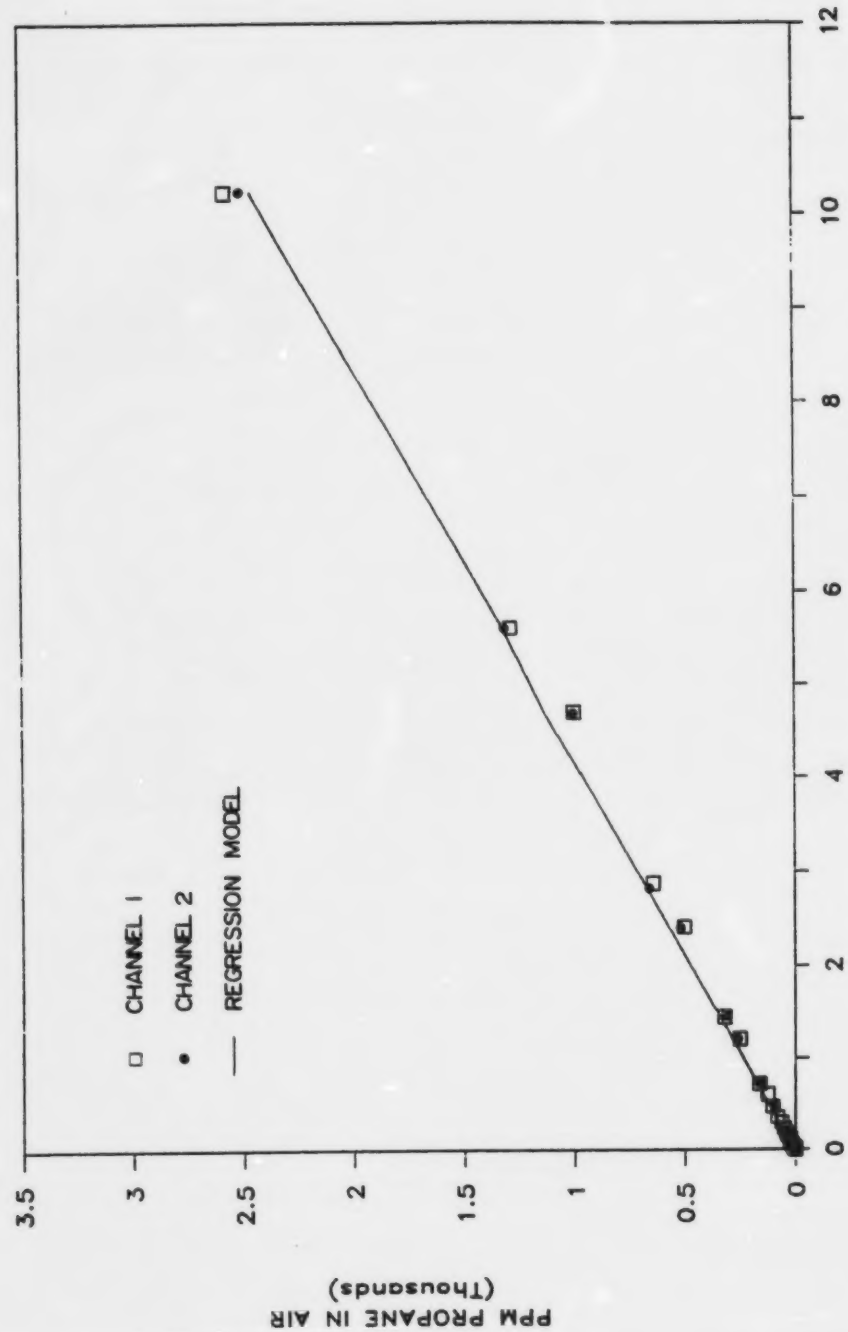

Figure 6. FID Calibration

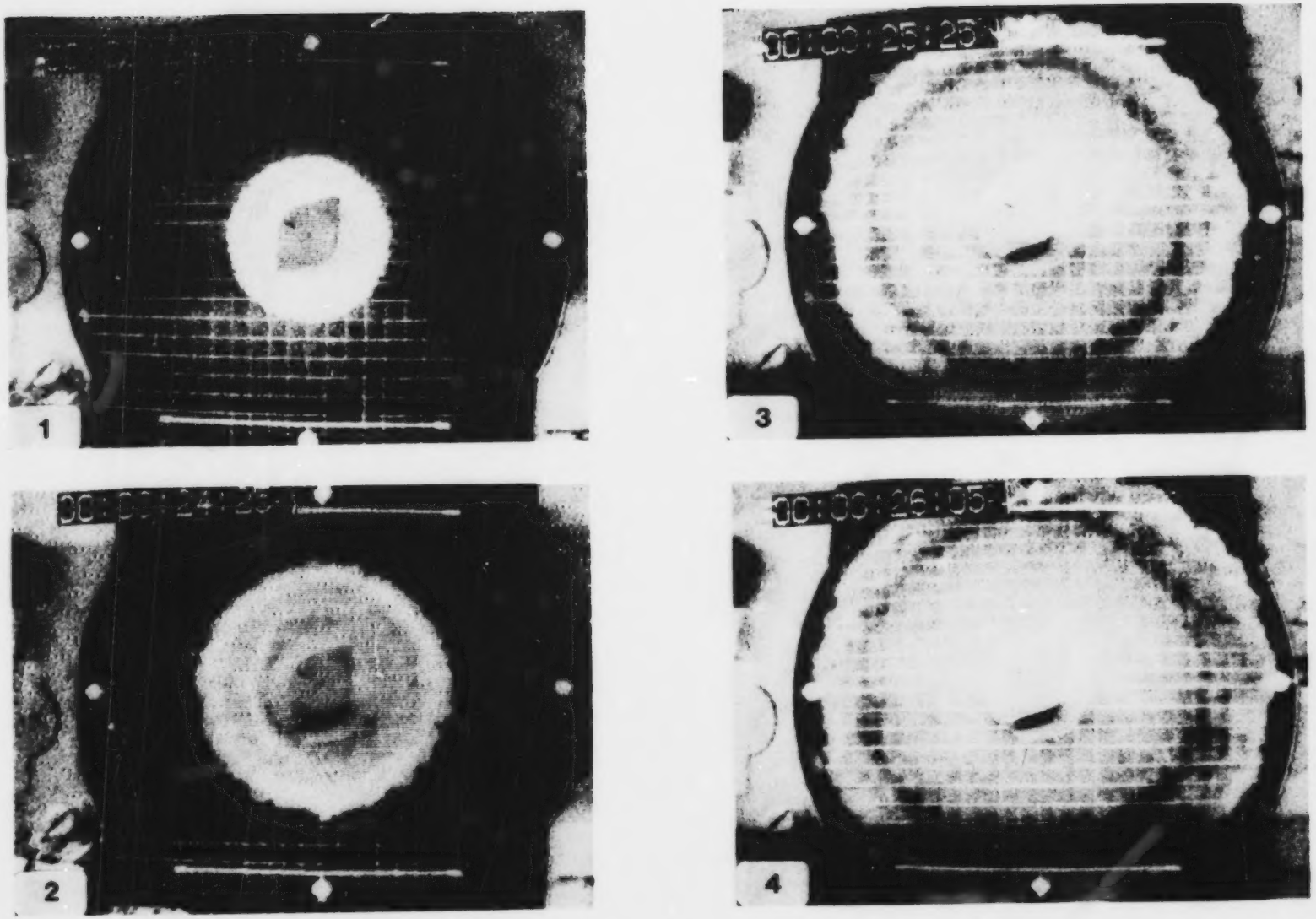

Figure 7. Release in calm wind – no obstacles

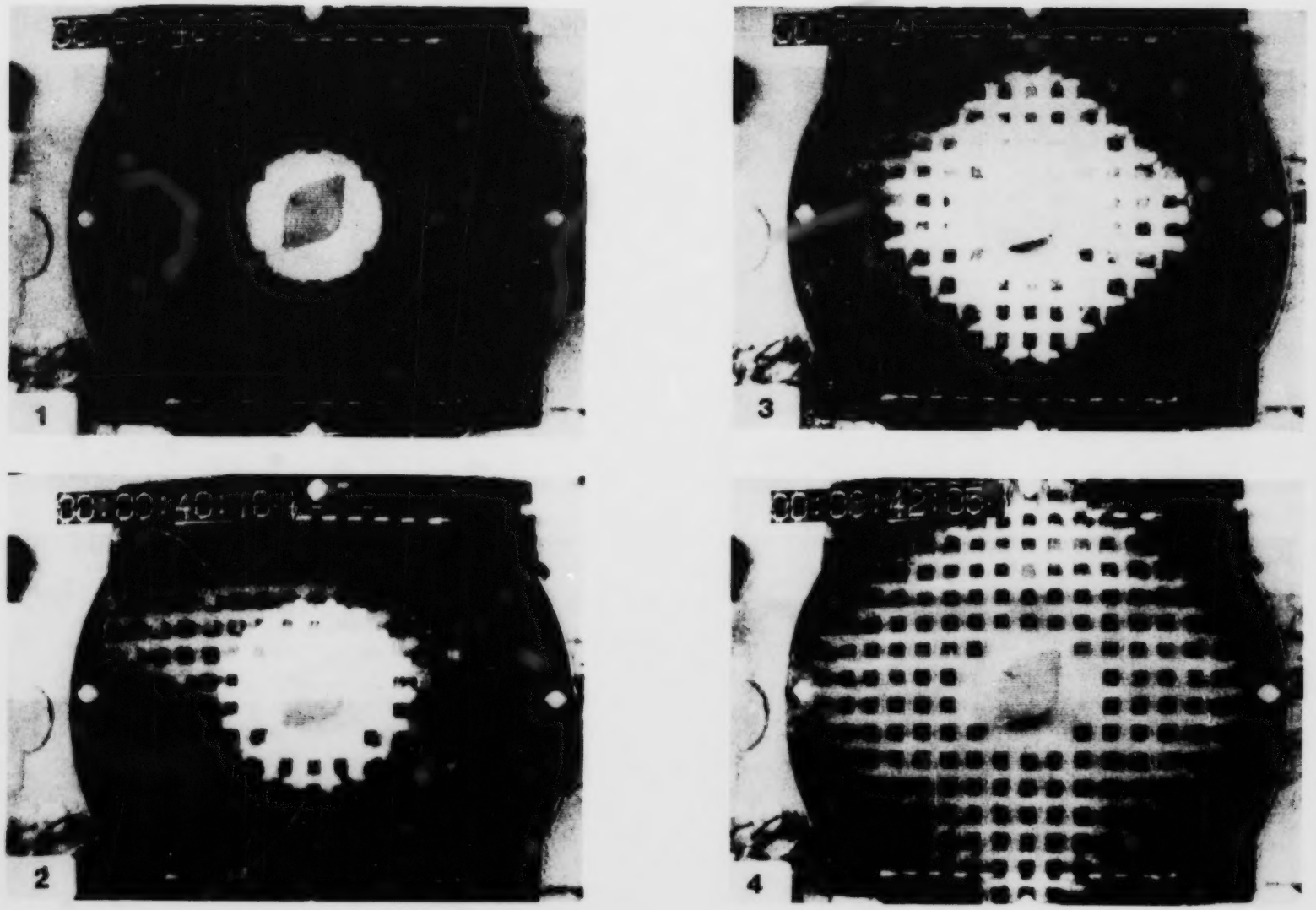

Figure 8. Release in calm wind – with obstacles

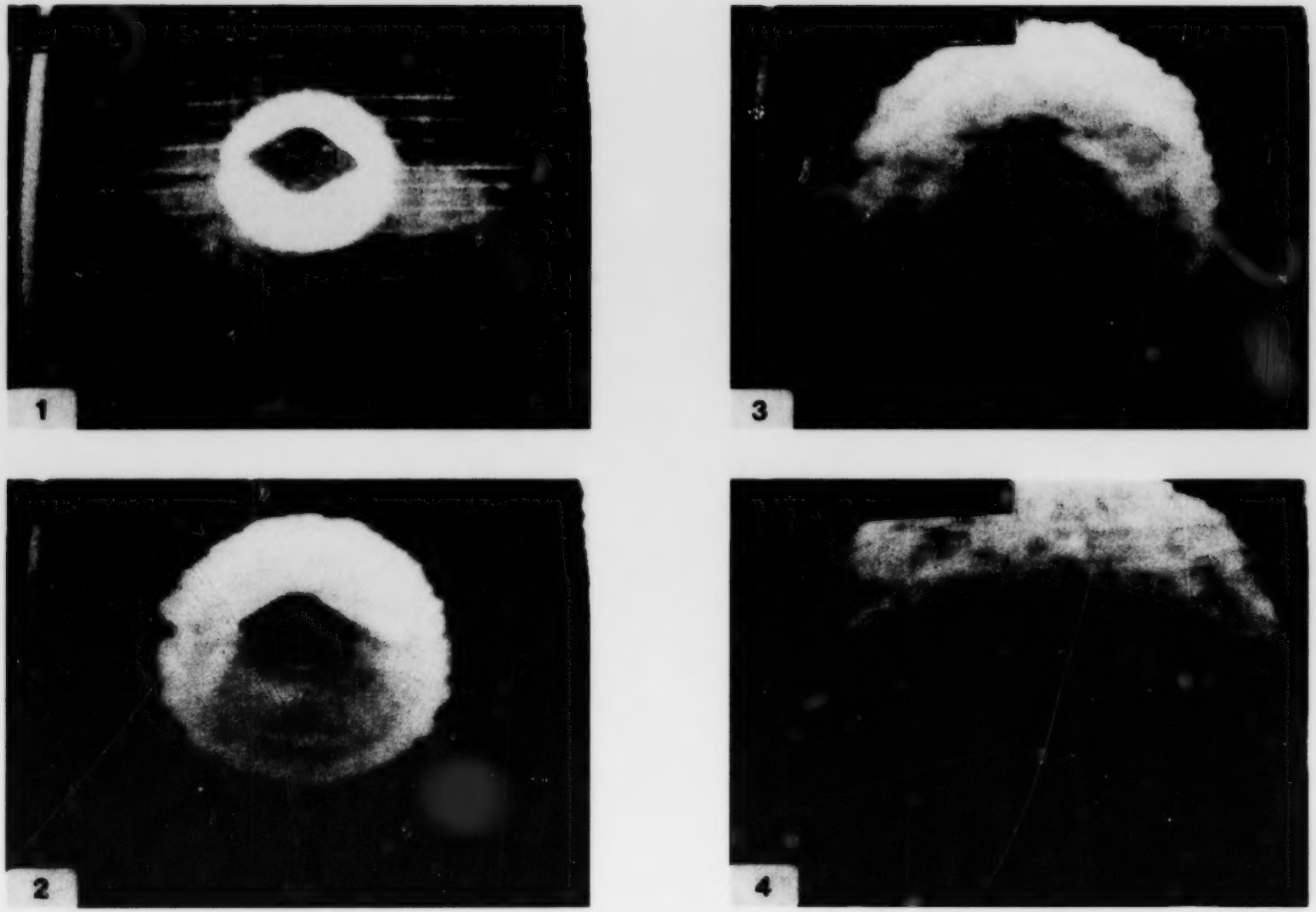

Figure 9. Release with 5 m/s wind – no obstacles

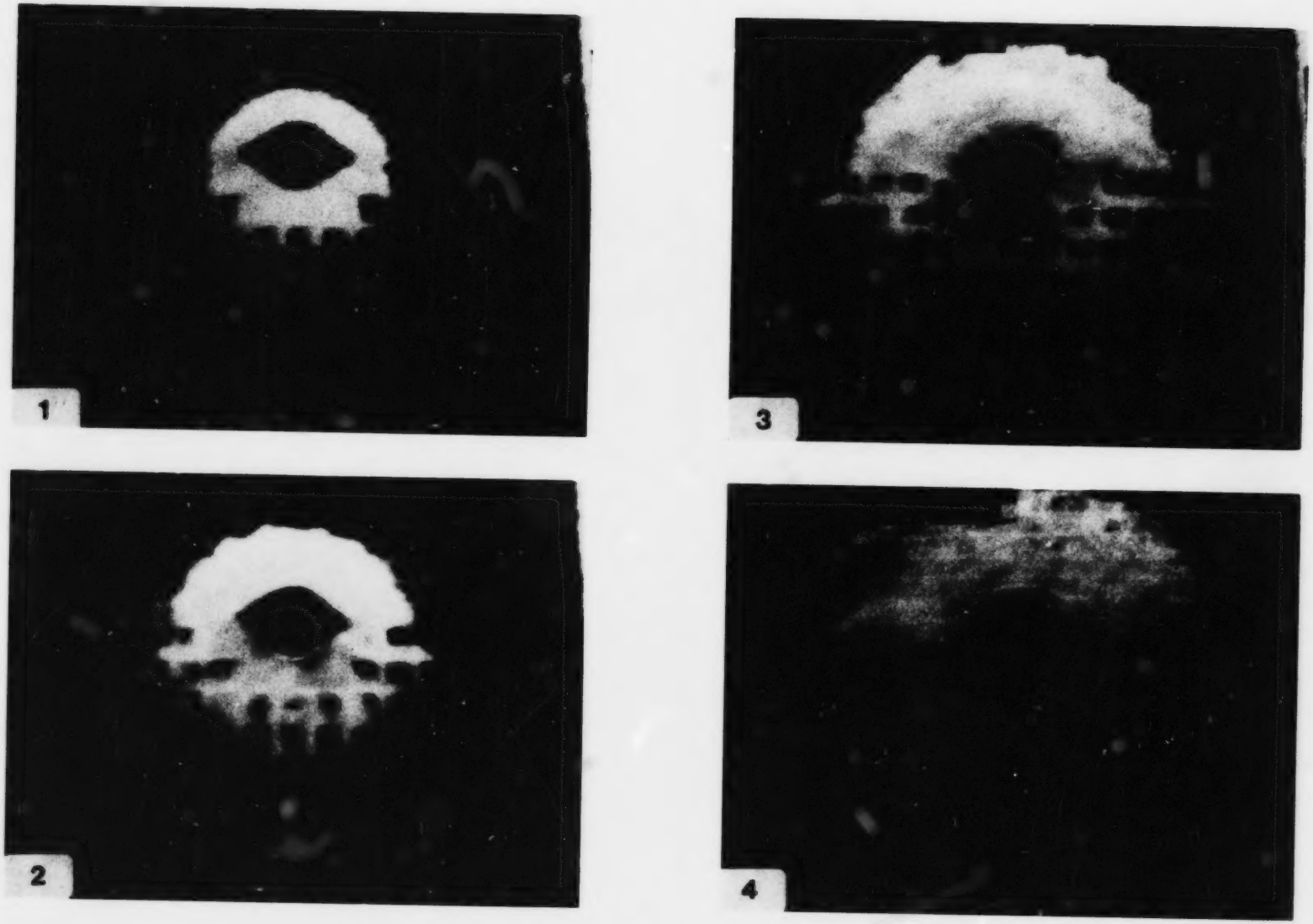

Figure 10. Release with 5 m/s wind – with obstacles

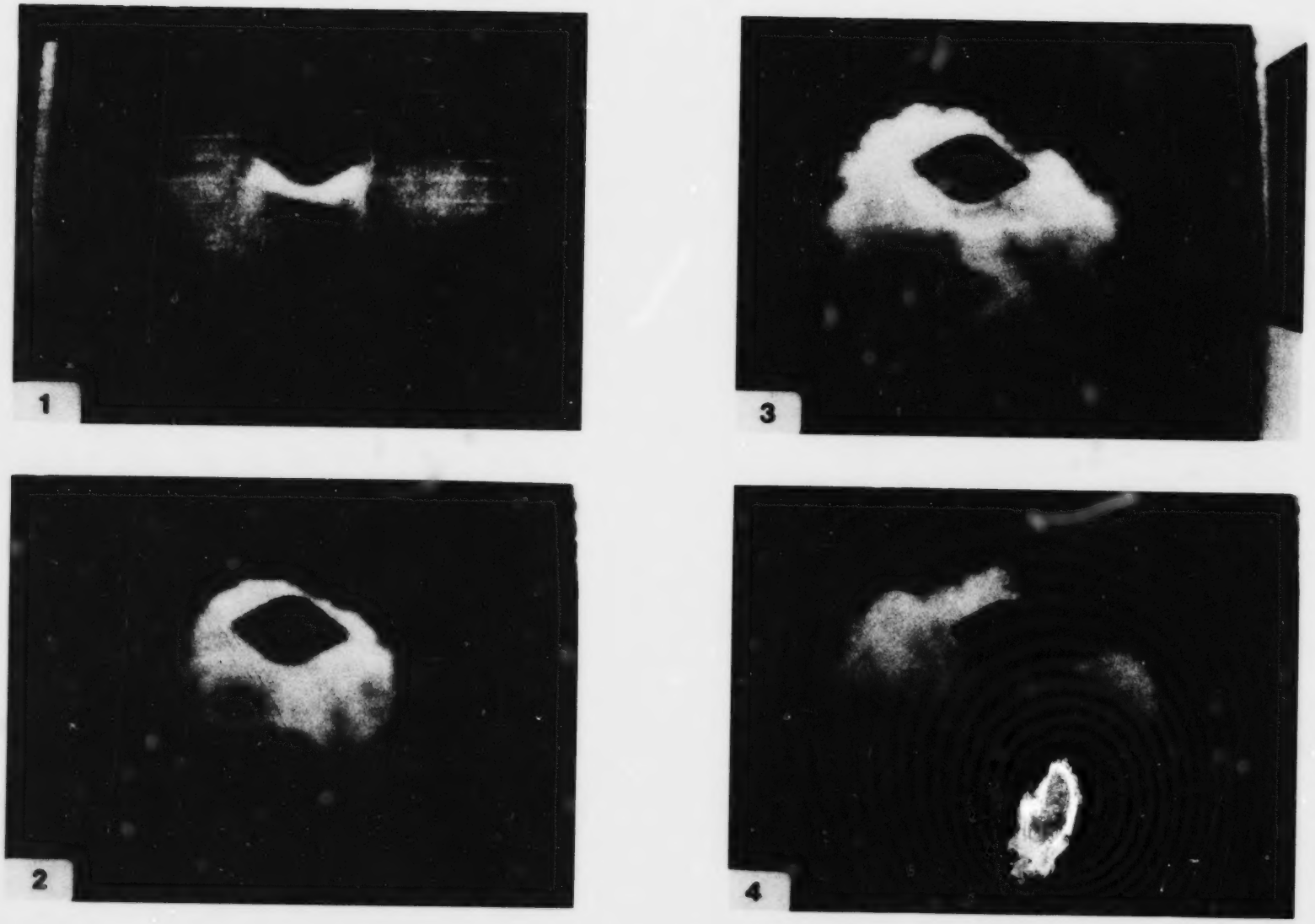

Figure 11. Release with 10 m/s wind – no obstacles

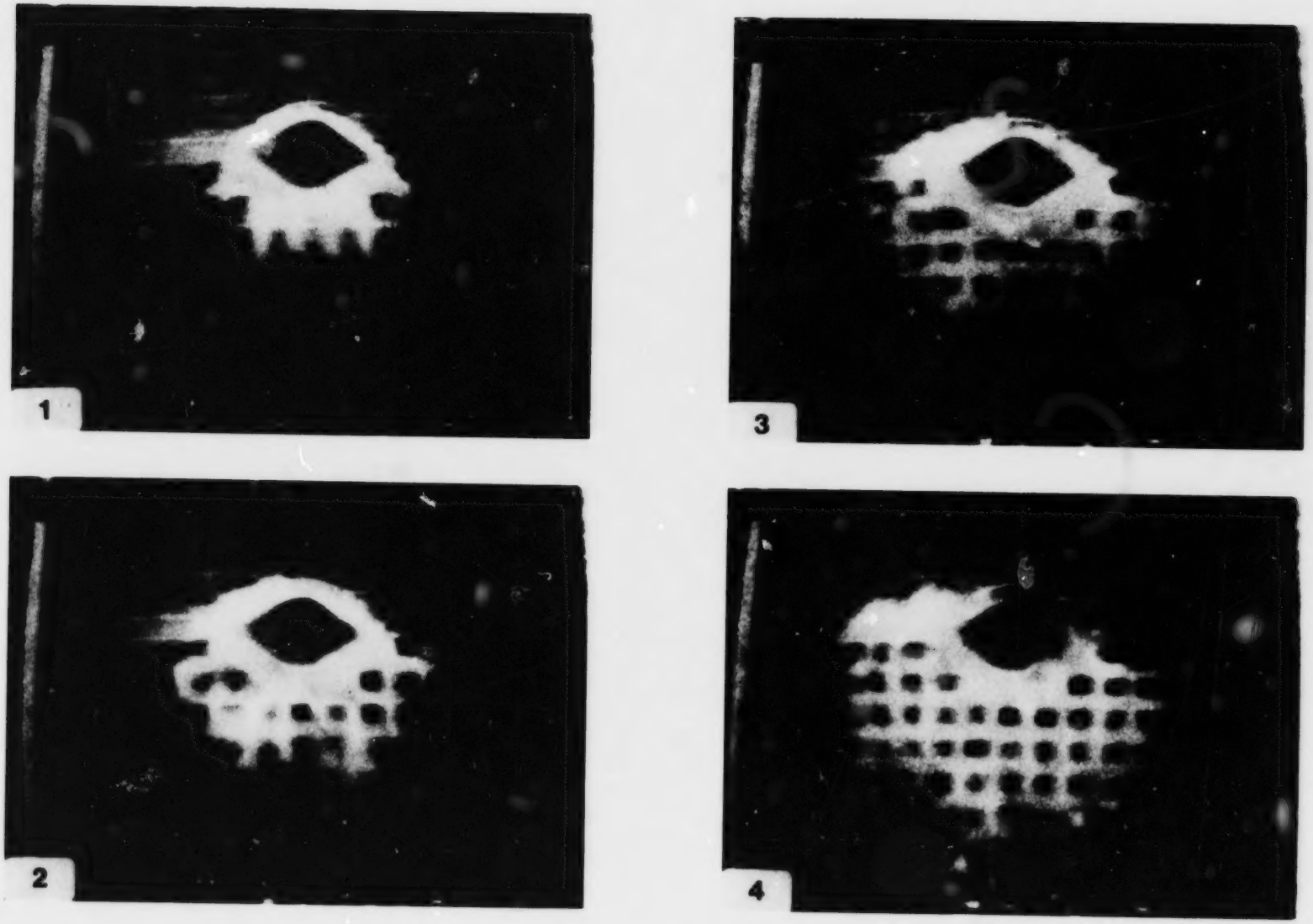

Figure 12. Release with 10 m/s wind – with obstacles

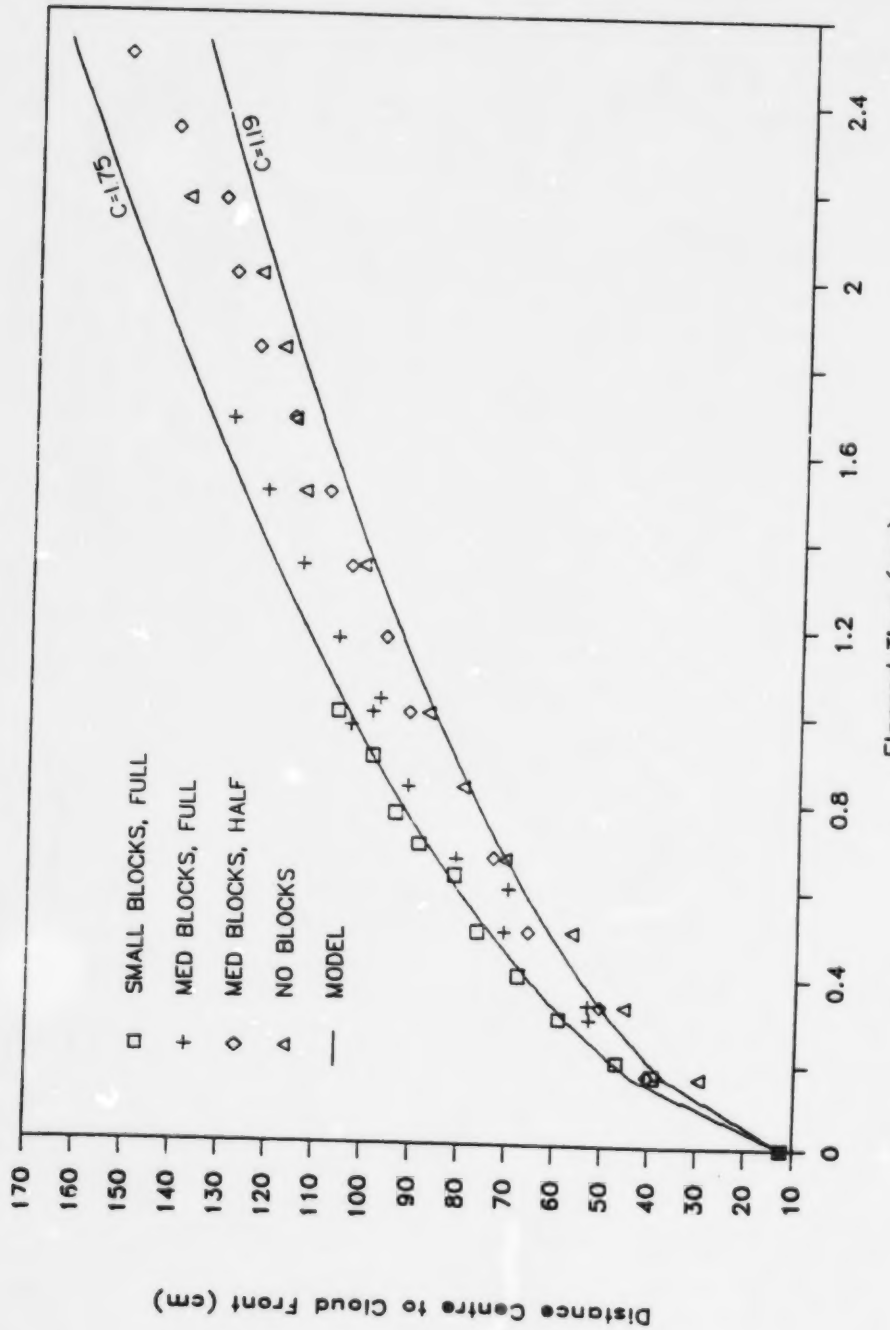

Figure 13. Cloud front flowing along corridor

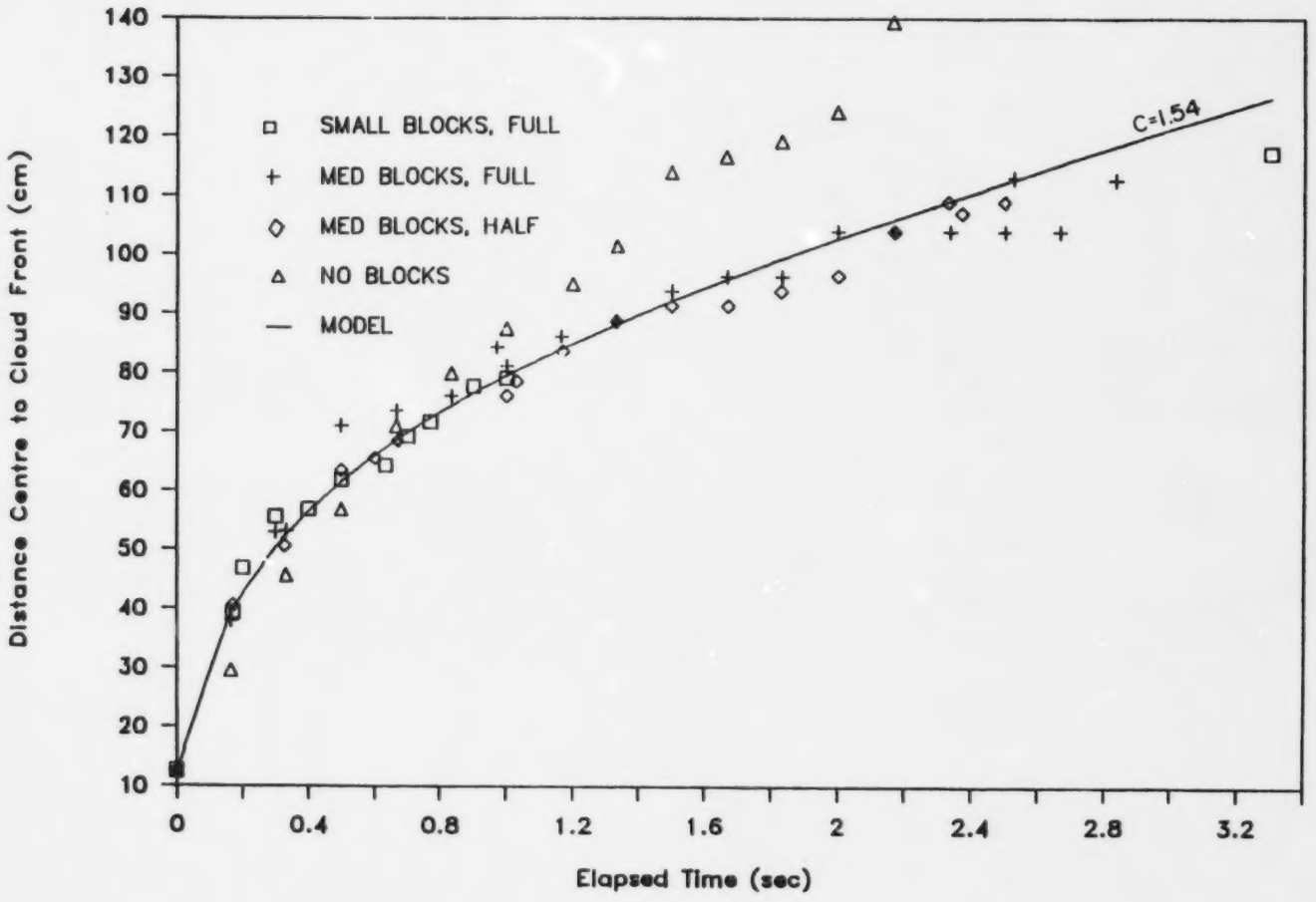

Figure 14. Cloud front flowing 45 deg from corridor

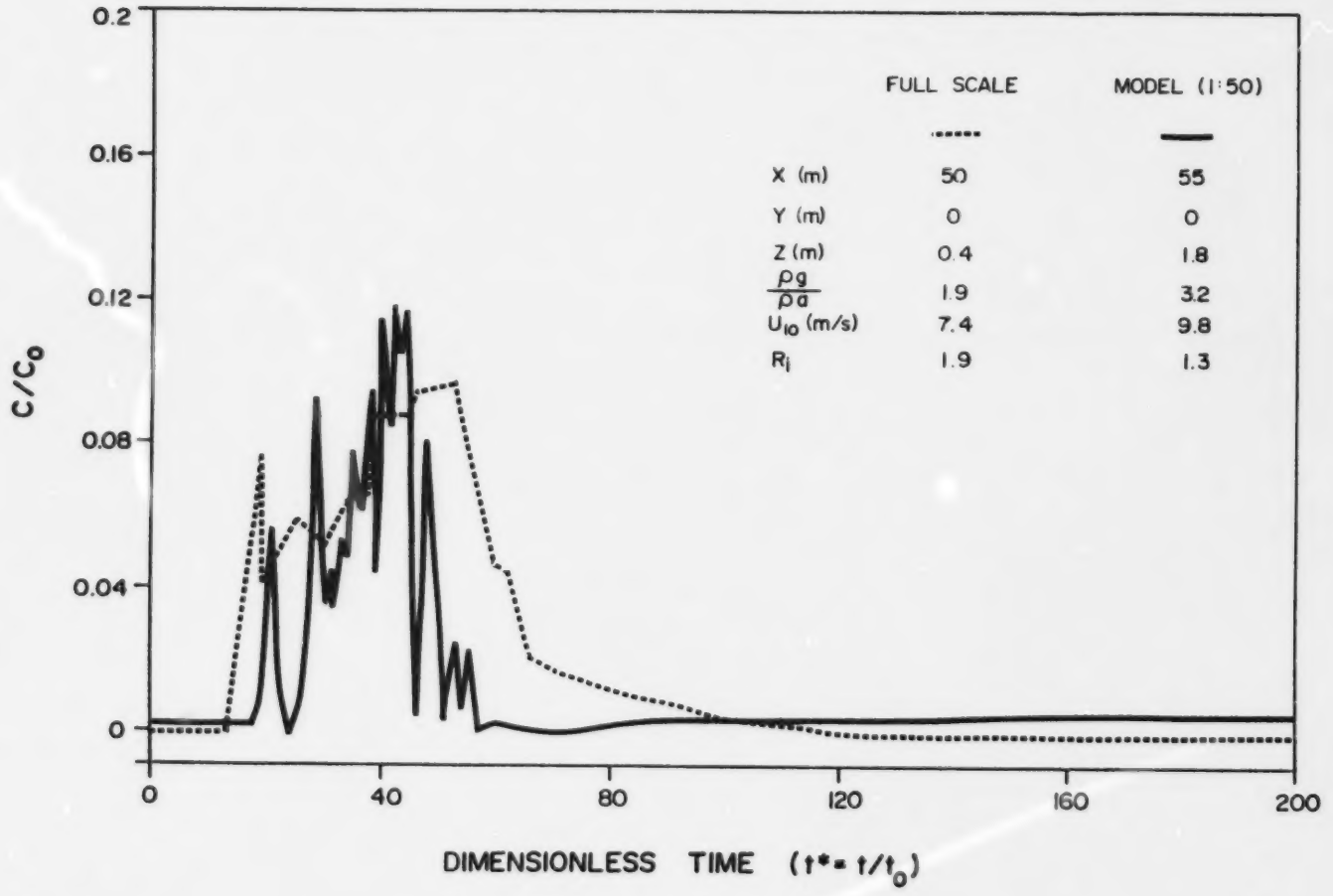

Figure 15. Model compared with full scale

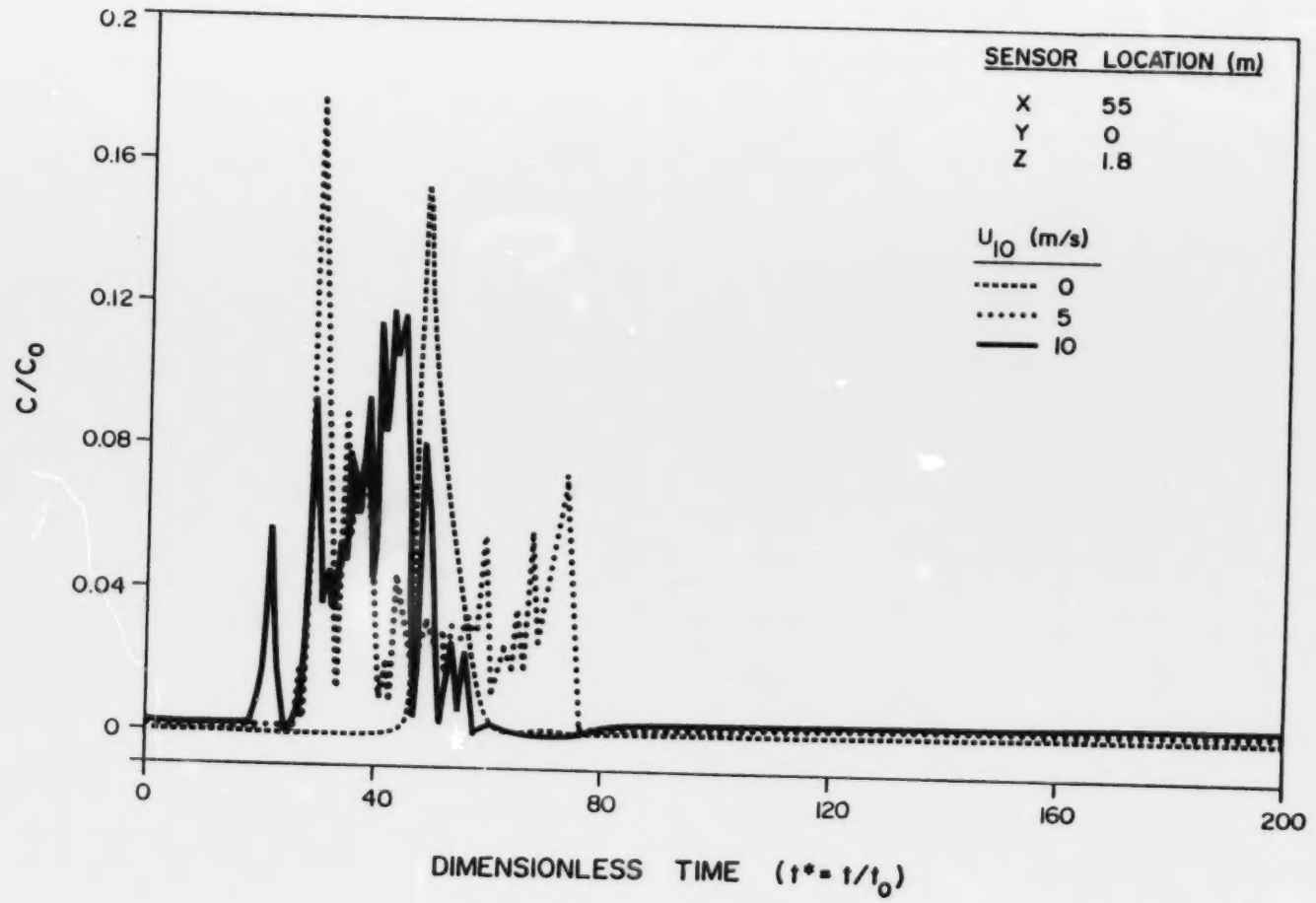

Figure 16. 1:50 Release – no obstacles

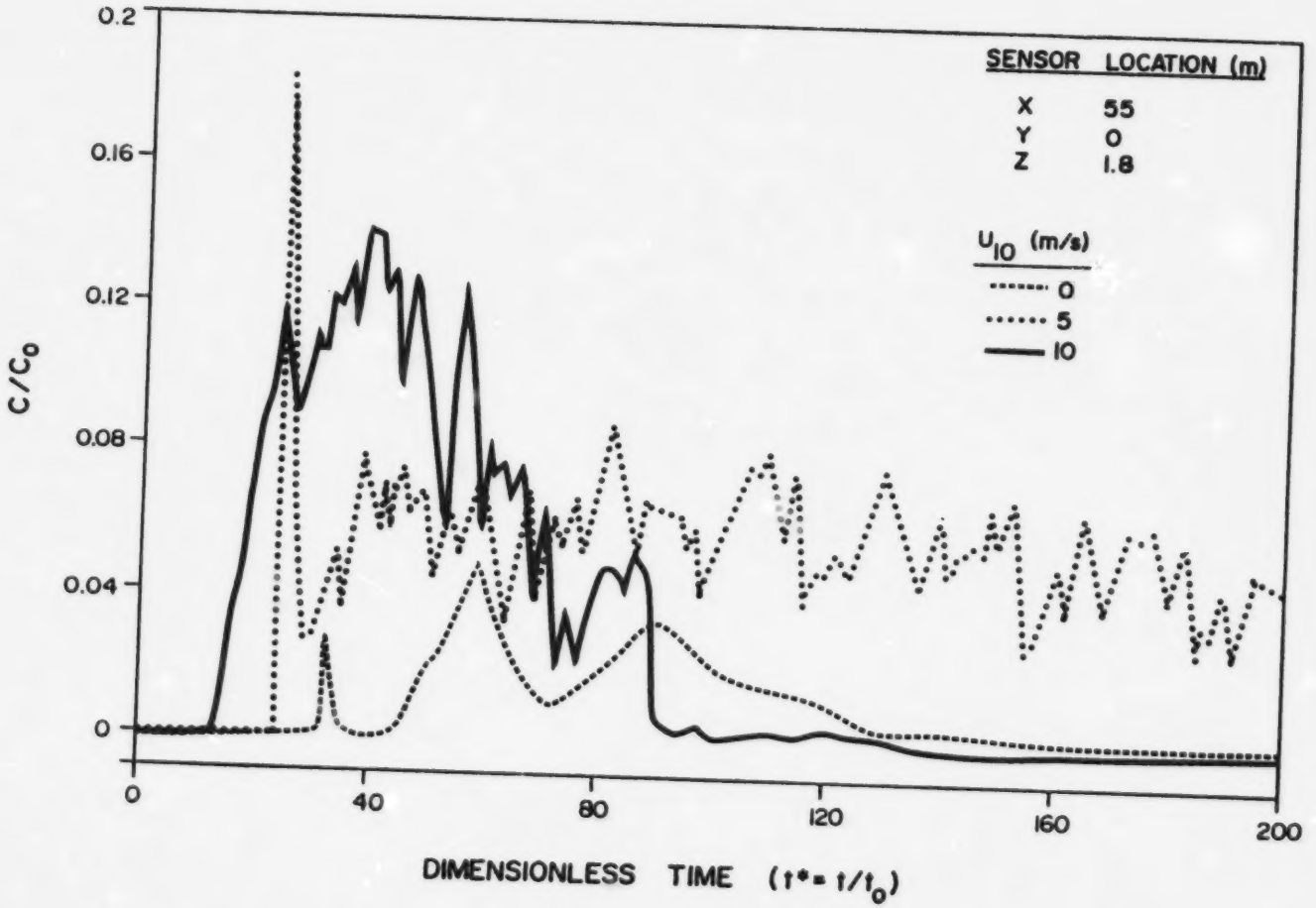

Figure 17. 1:50 Release – with obstacles

Rapid On-site Monitoring of Ambient PCB Levels During Clean-up and Destruction Activities

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Ontario Ministry of the Environment
Toronto, Ontario

Introduction

PCBs, or polychlorinated biphenyls, have been widely used in industrial and consumer products because of their chemical inertness, fire-resistance, high dielectric constant and low volatility at normal temperatures. During the early seventies, scientific evidence suggested that PCBs posed a hazard to health. Production of PCBs was banned in 1977, however, PCB filled transformers remain in service today. A 1985 Environment Canada PCB inventory reported an estimated 24,000 tonnes of PCB waste in Canada with nearly 10,000 tonnes located in Ontario. PCB waste is restricted from transportation and is stored on numerous sites throughout Ontario. In order to reduce the PCB inventory, Ontario has approved (Regulation 148/86) the use of commercial mobile PCB destruction units that chemically decontaminate mineral oils containing PCBs at levels less than 10,000 ppm.

The increased occurrence of PCB related incidents and destruction activities has made it necessary to develop an on-site monitoring technique to safeguard the residents of Ontario. During an emergency, such as an accidental PCB spill or uncontrolled fire, on-site monitoring results can be used to assist the site commander in taking an appropriate course of action. The technique adopted by the Ontario Ministry of the Environment, combines an automated short term adsorber (ASTA) with a mobile trace atmospheric gas analyzer (TAGA), a specialized mass spectrometer that allows direct air sampling and analysis. With this technology, on-site measurements of selected PCB isomer groups can be obtained at 2-minute intervals, providing immediate analytical information regarding the extent of environmental contamination.

Although the detection limits of this mobile technique, typically 20 ng/m^3 per isomer group, are higher compared with those of laboratory-based protocols, the ASTA/TAGA technique allows for rapid on-site analysis, as opposed to hours or days normally required for sample collection, preparation and analysis by traditional methods. When dealing with a potentially hazardous situation the immediate objective is to acquire air quality data, thus sensitivity may be sacrificed for expediency and safety. This paper will briefly describe the mobile PCB monitoring technique and its recent applications.

PCB Monitoring Methodology

For most chemical classes the sensitivity of the TAGA is extraordinary for determining trace levels of organic contaminants. However PCBs are one of the exceptions, because the absolute sensitivity is insufficient for real-time detection relative to the low guideline set by the Ontario Ministry of the Environment for PCBs (0.45 $\mu g/m^3$

for a half-hour sampling period). Thus a simple sampling device was required to concentrate the volatile PCBs while still retaining the capability of near real-time detection by the mobile TAGA unit. This device, known as an automated short term adsorber (ASTA), lowers the PCB detection limit by two orders of magnitude. The total sampling time is only 2 minutes and the subsequent analysis for selected PCBs is immediate.

The ASTA, shown in Figure 1, consists of two identical spiral tapered probes made of Chromel-A wire with a base diameter of 5/8 inches. These probes are coated with a thin layer of OV-17, a chromatographic stationary liquid phase. The dual probe assembly allows for trapping of PCBs with the top probe, while simultaneously conducting mass-spectrometric analysis on the bottom probe for the presence of PCBs. The positions of the two probes are interchangeable and their cycling time is controlled by the TAGA main frame computer.

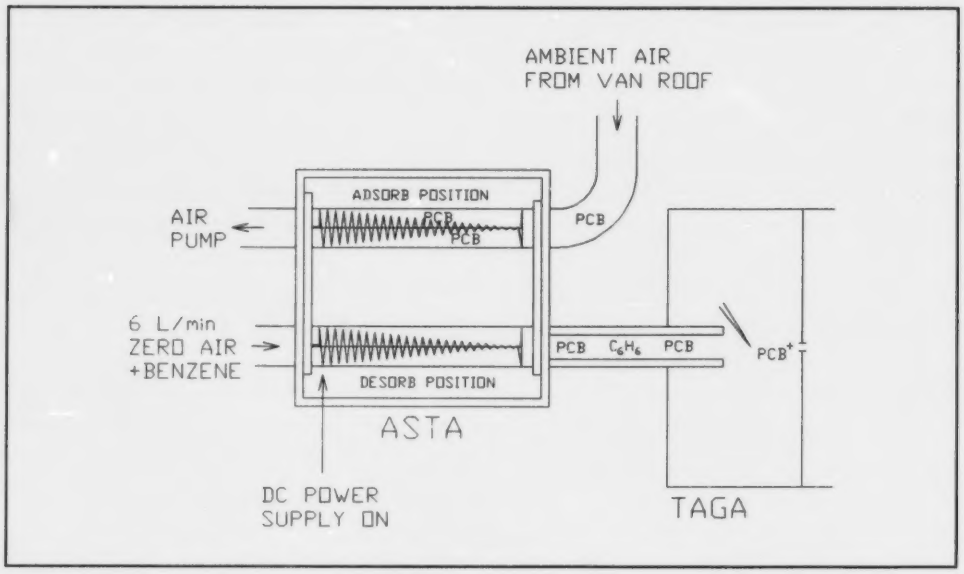


FIGURE 1: SCHEMATIC OF THE ASTA USED IN CONJUNCTION WITH THE TAGA PCB MONITORING TECHNIQUE

Ambient air is drawn at a flowrate of 100 l/min. from the mushroom-shaped inlet on the roof top through the glass tube plumbing to the adsorbing probe of the ASTA (see Figure 2). Gaseous PCBs present in the air stream are trapped by the OV-17 coated on the probe. The glass inlet tubing is wrapped with heating tapes to maintain the air temperature immediately downstream of the probe at 45°C. This temperature is critical to eliminate the adsorption of volatile compounds and to maintain maximum trapping efficiency of semi-volatile compounds. The total sampling time is 2 minutes and the sample volume is 200 litres of ambient air. After 2 minutes the probes switch positions and 24 volts DC is applied to the probe, which is now in the desorption position, causing the probe temperature to increase rapidly to approximately 300°C. Any PCBs adsorbed by the OV-17 will vaporize and travel directly into the ion source of the TAGA. The

carrier gas is comprised of 6.6 l/min. of ultra pure zero air and 100 ppm of benzene. The benzene serves as a chemical ionization reagent producing molecular PCB ions which are directed into the vacuum chamber and rapidly mass analyzed by the quadrupole mass filter. The time to complete one full cycle, or analysis, is 2 minutes and 8 seconds. A half-hour concentration of PCBs is determined by simply averaging 15 consecutive 2-minute samples. The entire procedure is computer automated.

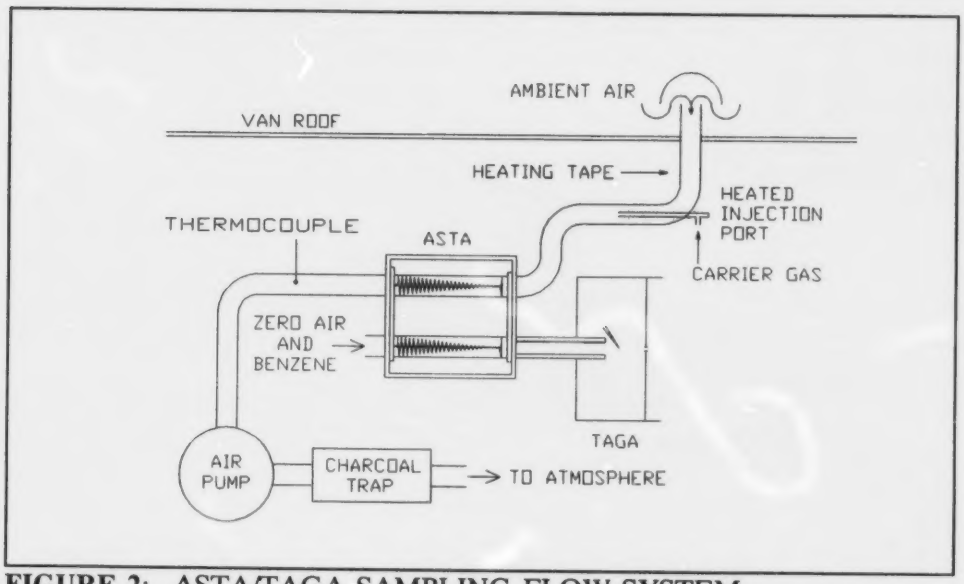


FIGURE 2: ASTA/TAGA SAMPLING FLOW SYSTEM

Calibration of the system is accomplished by injecting a standard PCB isooctane solution upstream of the adsorption probe. The PCB standard is injected via a syringe pump through a heated injection port set at 300°C. The injected PCB solution is rapidly vaporized, mixed with the ambient airflow, and carried past the adsorption probe. Four different PCB concentrations, over the range of 0.11-1.2 $\mu g/m^3$, are generated by varying the speed of the motorized syringe drive. Each PCB calibration level is repeated four times. The M+ and M+2 ion pairs corresponding to a PCB isomer are measured and compared to the natural abundance of the ^{35}Cl and ^{37}Cl isotopes. The on-board computer plots the calibration curves for each PCB congener monitored. Figure 3 shows examples of the calibration plots for the di- and trichlorobiphenyl isomer groups. The response factor(s) for a PCB isomer group is determined from the slope of the concentration response curve of the representative congener. The standard deviations of the background, or upwind measurements are used to determine the analytical detection limits.

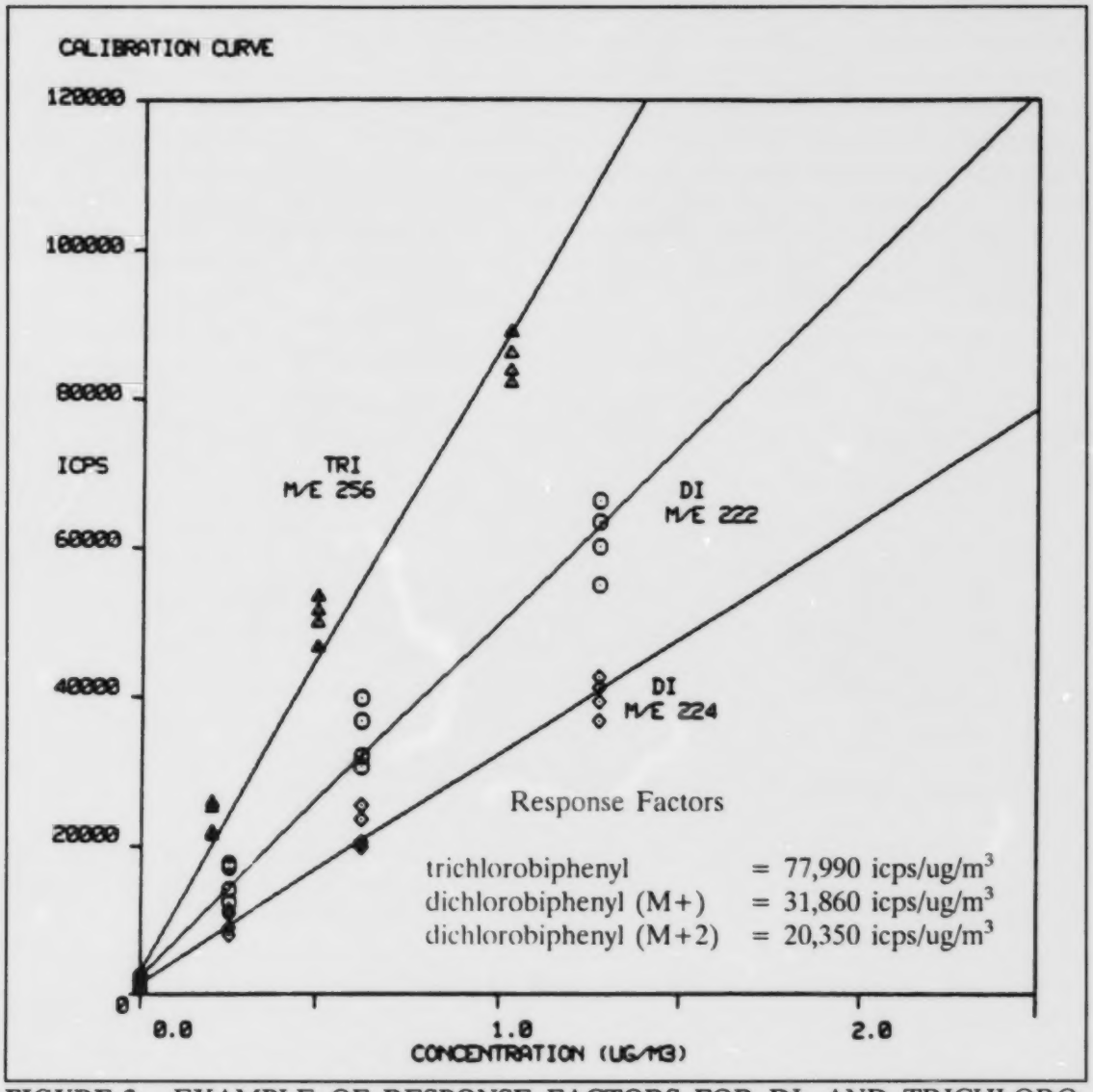


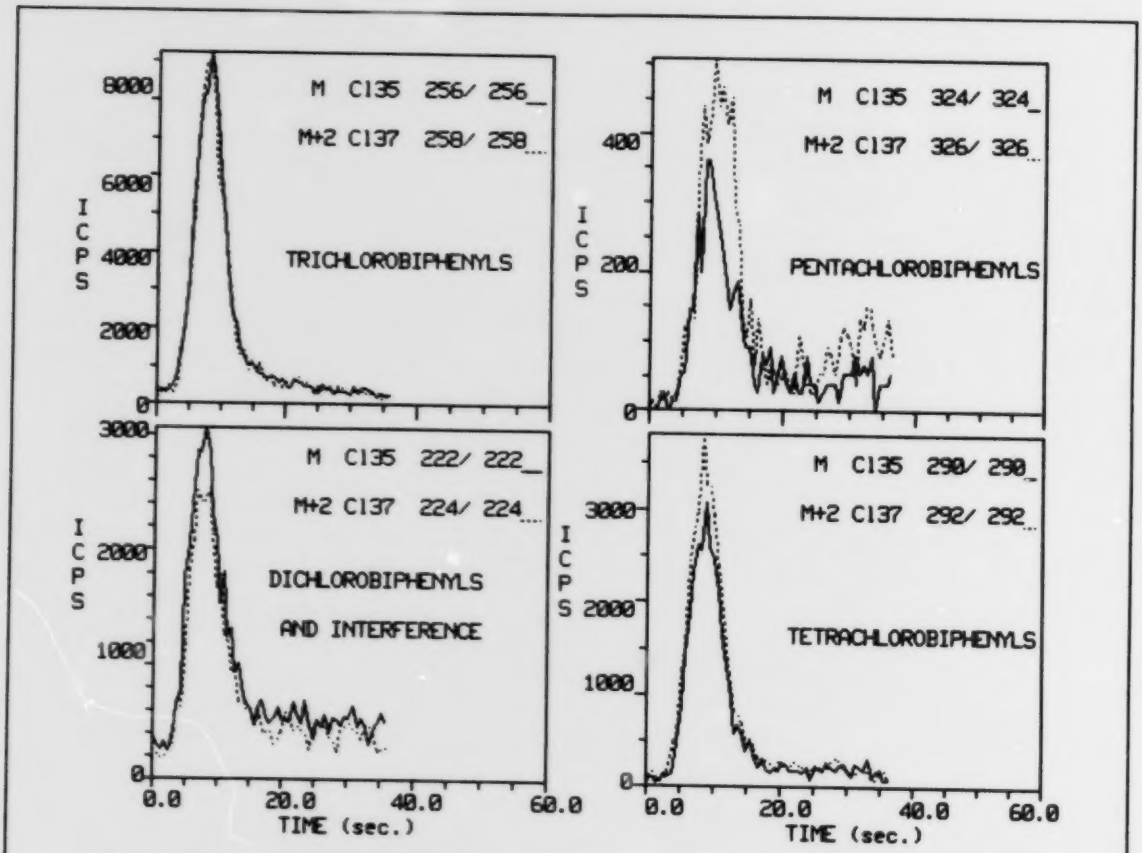
FIGURE 3: EXAMPLE OF RESPONSE FACTORS FOR DI- AND TRICHLORO-BIPHENYLS USING ASTA/TAGA MONITORING TECHNIQUE

During each survey day calibrations are performed at upwind locations to determine the response factors and the detection limits for the selected PCB isomer groups. Also ambient air samples are spiked periodically to ensure that daily response factors are within their set limits. Typical detection limits for the di- to pentachlorobiphenyls generally range from 0.01 to 0.05 $\mu g/m^3$ per isomer group.

Data Interpretation and Analysis

During the first 12 seconds of the desorption cycle the PCBs are thermally driven

from the OV-17. Heat is maintained for another 20 seconds to ensure a clean probe for the next sampling period. Meanwhile the PCB desorption curves are generated by the computer providing the following information for the survey scientist: the time of the desorption peak; the integrated area for each desorption curve; ratio of the ion pairs; net PCB concentrations; and the signal to noise ratio for each isomer group. The current software is programmed for 8 ion masses allowing for the simultaneous measurements of 4 PCB isomer groups (see Figure 4).



MP/MD	MAX. INT	TIM. MAX	INT. IONS	NET	CONC	RATIO TO MP/MD		THEOR.
222/ 222	3053.	8.40	17143.	14691.	0.39	1.283	224/ 224	1.540
224/ 224	2520.	9.12	13994.	11452.	0.47	0.780	222/ 222	0.650
256/ 256	9213.	8.56	46335.	43368.	0.60	1.056	258/ 258	1.030
258/ 258	8906.	8.64	43545.	41069.	0.62	0.947	256/ 256	0.975
290/ 290	3067.	9.36	14284.	12730.	0.23	0.818	292/ 292	0.769
292/ 292	3800.	8.80	17271.	15562.	0.23	1.222	290/ 290	1.300
324/ 324	360.	9.52	1707.	1303.	0.10	0.620	326/ 326	0.615
326/ 326	507.	10.24	2662.	2099.	0.11	1.612	324/ 324	1.626

FIGURE 4: EXAMPLE OF TAGA DATA FOR PCB ANALYSIS. Concentrations are in $\mu g/m^3$. Note the ratio for isotope 222/224 dichlorobiphenyl is mismatched indicating the presence of chemical interferences at masses 222 and/or 224.

For most applications the di-, tri-, tetra- and pentachlorobiphenyl isomer groups are targeted. These are the most common isomers found in industrial applications. Also, PCBs with higher degrees of chlorination possess lower vapour pressures, consequently they are less likely to be detected by the ASTA/TAGA technique. Confirmation of PCB presence is based on the following criteria:

i. Isotope pair ratios - the measured isotope pair ratios must be within +/- 10% of the theoretical values;
ii. Isotope pair concentrations - the PCB levels determined for an isotope pair must be within 20%;
iii. Desorption peaks - the desorption curves for an isotope pair must peak simultaneously;
iv. Signal to noise ratios - the S/N ratio for each PCB desorption curve must be greater than three.

If the above criteria for PCB confirmation are not satisfied it suggests that a chemical interference is present at the same ion mass of the target PCBs, and accurate quantitation is not possible for the corresponding isomer group.

Field Applications

The ASTA/TAGA PCB monitoring technique has proven to be useful to screen the ambient air for PCBs during the following activities:

a. PCB site clean-up - to monitor the ambient concentrations of airborne PCBs during the removal of contaminated soil;

b. Mobile PCB destruction - to monitor the emissions from mobile PCB destruction units;

c. PCB storage facilities - to monitor fugitive emissions of gaseous PCBs in the vicinity of PCB storage areas;

d. Emergency monitoring - to determine ambient levels of PCBs associated with PCB spills and fires.

Table 1 summarizes the findings of a survey conducted in Southwestern Ontario during a two week period in October 1984. The survey objective was to monitor the ambient air for selected PCBs during the relocation of PCB contaminated soil to a clay vault. Prior to breaking ground, gaseous PCBs was not detected near the site. During the excavation of soil contaminated with PCBs, the TAGA recorded 2-minute averaged concentrations up to 4 $\mu g/m^3$. After all the contaminated soil had been safety stored in a capped vault, the ambient PCB levels were below the detection limit of 0.04 $\mu g/m^3$.

DAY	NO. OF SAMPLES	AVE. TOTAL PCBs ($\mu g/m^3$)	COMMENTS
1	5	0.07	Prior to digging
2	10	3.9	Excavation of ditch
3	30	0.73	Asphalt removed
4	20	3.0	Soil near tanks
5	40	0.72	Soil SE corner
6	40	1.0	Large pile SE corner
7	100	0.21	Large pile
8	10	0.04	Capping vault

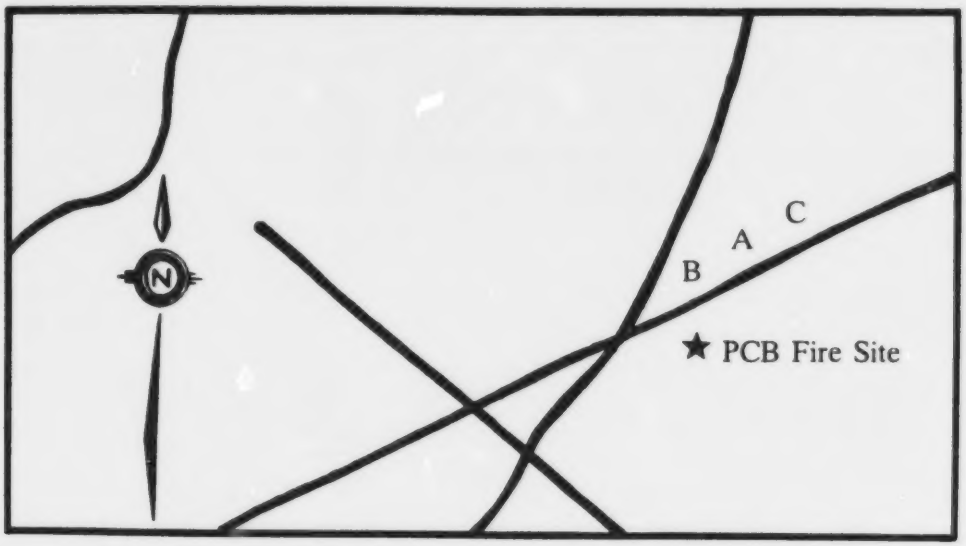
TABLE 1: TAGA SURVEY DATA TAKEN DURING PCB SOIL EXCAVATION ON OCTOBER 1984.

The results of a survey conducted in September 1987 are presented in Table 2. During this particular survey the mobile TAGA unit screened the ambient air for selected PCBs during the decontamination of 2,000 litres of transformer oil containing 61 ppm PCBs. The PCBs were chemically destroyed on-site by a mobile PCB destruction unit over a period of five hours. During the entire monitoring period the ambient PCB concentrations were below the analytical detection limits, which ranged from 0.07 to 0.17 $\mu g/m^3$ for the di- to pentachlorobiphenyls. Concurrent with the TAGA measurements, ambient PCBs were determined by traditional methodology, that is, solid absorbent cartridge sampling followed by gas chromatographic analysis. PCBs were not detected by either analytical method.

NO. OF SAMPLES	AVE. TOTAL PCBs ($\mu g/m^3$)	COMMENTS
30	ND	Upwind background
15	ND	Downwind, prior to start
15	ND	DW, transferred PCB oil
15	ND	DW, sodium added to oil
60	ND	DW, destruction on-going
15	ND	DW, destruction completed

TABLE 2: TAGA SURVEY DATA DURING PCB DESTRUCTION IN SEPTEMBER 1987. ND = not detected.

Recently the mobile TAGA unit was involved in emergency monitoring of PCBs following the destruction of a PCB warehouse by fire. Figure 5 shows some of the ambient air PCB data obtained at various sampling locations in the immediate vicinity of the fire site. The data clearly indicates the importance of the selection of sampling sites relative to the source and the wind direction. PCBs were only detected directly downwind of the fire site on an adjacent highway. The highest PCB levels were observed during periods of steady winds, despite of the fact that the sampling site was farther from the source. It is noteworthy that the PCB measurements were made six days after the fire had been extinguished. The existence of airborne PCBs was believed to be a result of clean-up activities occurring at the site.



LOCATION	DISTANCE FROM SITE	WIND DIRECTION	30-MIN. AV. PCBs(ug/m^3)
A	100m	SW,variable	.21
B	0m	SW,variable	ND
C	200m	SW	.56

FIGURE 5: MAP OF TAGA MONITORING SITES AND AVERAGE CONCENTRATIONS NEAR THE WAREHOUSE FIRE SITE. (Detection limit = 0.07 $\mu g/m^3$ for total PCBs)

Summary

The Ontario Ministry of the Environment has developed a PCB analysis technique which utilizes the real-time monitoring capabilities of their mobile trace atmospheric gas analyzer (TAGA) systems. An automated short term adsorber (ASTA) interfaced with the TAGA's direct air inlet serves to trap and concentrate PCBs prior to mass spectrometric analysis. With the introduction of the ASTA, the TAGA's analytical detection limits for PCBs were reduced to levels below the Ministry's regulatory guideline for ambient PCBs ($0.45\mu g/m^3$ for a 30 minute sample).

Since 1985, the ASTA/TAGA technique has been used in nine mobile air monitoring surveys where the potential for PCB release existed; mobile PCB destruction processes, removal of PCB contaminated sediments, and PCB spillage following the destruction of a storage facility by fire.

NECESSITY FOR AND AVAILABILITY OF TRAINING FOR DRILLING PERSONNEL. R.D. TURPIN, M.E. MORTENSEN, U.S. ENVIRONMENTAL PROTECTION AGENCY ENVIRONMENTAL RESPONSE TEAM, EDISON, N.J., 08837 AND M.J. O'NEILL, ROY F. WESTON, INC., REAC, EDISON, N.J., 08837

INTRODUCTION

Since late 1986, there has been a serious shortage of environmental drilling services for efforts at toxic waste sites and spill activities. This shortage has been caused by a sequence of events pertaining to federal environmental programs. Firstly, Superfund was renewed at a much higher level of funding in 1986 (9.5 billion dollars, plus an additional half billion more towards the Underground Storage Tank (UST) program). This has increased EPA's site activities which in turn has raised the demand for drilling services. Secondly, OSHA published an interim final rule in December 1986 and a Final Rule in March 1989, requiring all workers at hazardous waste operations to have 24 to 40 hours of initial training in issues relative to hazardous waste site health and safety. In addition, one needs on-the-job training and 8 hours of annual refresher training. Such training necessitates the dedication of additional expenditures on the part of drilling firms in the form of man-days and tuition.

The objectives of this paper are to identify a source of hazardous waste site health and safety training; and demonstrate through four (4) case histories the necessity for hazardous waste health and safety training.

TRAINING

Currently, hazardous waste health and safety training courses are available from various sources such as: private sector, State Agencies, Universities, Labor Unions, and Federal Government. The U.S. Environmental Protection Agency's Environmental Response Team (ERT) has offered such courses since 1979. The ERT was established in October 1978 to provide technical assistance and training to Federal On-Scene-Coordinators (OSC), Regional Response Team (RRT), National Response Team (NRT), EPA Headquarters/Regional Offices, and other government agencies in various environmental emergency issues such as chemical spills and hazardous waste operations.

Presently, ERT offers seven courses throughout the United States which range from Air Monitoring to a Hazardous Waste First Response Operations Course. For additional information contact:

U.S. Environmental Protection Agency
Environmental Response Branch
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7537

BACKGROUND

Over the years, ERT has observed some reluctance from drillers to work on government projects when work for private interests has been readily available. The complaints have ranged from delays in payment to excessive training requirements and extreme levels of responsibility for future site conditions. However, the majority of well drillers involved in Superfund sites are subcontractors to private consulting or engineering firms with EPA contracts. In this capacity then, terms of payment and responsibilities of the drillers are similar to private contract work.

ERT has also observed that few drillers have the necessary training or medical monitoring required for work at hazardous waste sites. The additional health and safety requirements for working on hazardous waste operations make it even less attractive to typical water well drillers. We feel well drilling is a dangerous occupation without the addition of hazardous materials. How many experienced drill crews do you know with missing finger(s)? At Superfund operations, employees risk the additional hazard of exposure to toxic chemicals.

When soil contamination is present, the chance for inhalation of dust particles is very real. Additionally, contaminated groundwater presents a risk of contact from splashs or inhalation of volatile vapors. Both of these situations necessitate the use of protective clothing and respiratory protection. The use of such equipment can make the drill site more complicated and distract employees attention from the moving parts of the drill rig. The challenging work site conditions of a drill rig on a hazardous materials site necessitate additional training in the use of protective gear, and on-the-job supervision of junior employees.

CASE HISTORIES

The following four case histories demonstrate the various hazards surrounding a drill rig and the importance of a dynamic health and safety training program for personnel involved in drilling operations. The first two case histories appear to be minor in comparison to the other two tragic accidents. All are equally useful in demonstrating the ramifications of ignoring or not being familiar with standard safety procedures which should be a major component of all training programs.

Case History #1

The accident illustrated in this case involved a very minor incident which if treated immediately, would not have presented a significant hazard.

The drilling operation was part of a Remedial Investigation (RI) at a Superfund site on a National Priorities List (NPL) in Tennessee. The drilling program consisted of the installation of 12 wells and 8 soil borings using hollow-stem augers and continuous split spoon sampling. Work started in February and was planned to end sometime in April. The

work schedule consisted of 10 to 12 hour days starting at 6:30 am. The accident occurred in late February. At the time of the accident, the crew had just completed a shallow well, and were starting to grout the casing.

The mixing of grout involves the creation of a slurry material by the addition of cement and bentonite to circulating water. During the mixing process, hazards presented to employees include splashes of grout, and inhalation of silica dust which is present in the cement and bentonite. Respiratory protection is seldom used due to the short duration of exposure. Likewise, proper eye protection is often neglected.

The specific accident involved a splash of grout material into a laborer's ear. The individual responded by "clearing" his ear with his finger. No attempt to flush the ear canal was made immediately following the incident. Neither the laborer's supervisor nor the Site Safety Officer was made aware of the accident.

Two days passed before the individual complained of an ear ache and revealed the details of the incident. At that point, he was taken to a physician who removed the grout, irrigated the ear canal and diagnosed a middle ear infection. Medication was prescribed and the employee remained out of work for two days.

Case History #2

The scenario surrounding this incident involved a splash hazard also, and emphasizes the need to be familiar with daily checkout procedures and the location of emergency equipment. Personnel were dressed in an upgraded Level D protective ensemble which included: Tyvek coveralls, nitrile gloves, and latex boot covers. Given the extreme cold temperatures (10^{0}-20^{0}F), personnel had donned additional layers of clothing in the form of insulated coveralls, gloves, and long underwear (Note: ERT does not recommend drilling operations below 20^{0}F).

The drilling operation was part of a RI program at a Superfund site in West Virginia and included the installation of eight well couplets. Work started in January and was scheduled to last 5 months. The daily work schedule consisted of 10 hour days with a break in mid-morning and mid-afternoon. The accident occurred in February. A hollow stem auger rig, equipped with a split spoon sampler was being utilized.

The accident occurred during decontamination of equipment following completion of the third well. The extreme cold temperatures had severely hampered progress, and drilling operations were proceeding at a slow pace. One employee was performing the 100% hexane rinse over a galvanized tub. Another employee dropped a sampling device into the hexane rinse tub. The employee who was bent over the tub received a splash of hexane in the eye. His immediate reaction was to rub his eye with his hand. When he decided to use the emergency eye wash positioned near the decontamination line, it was inoperative. The extreme cold temperatures had caused the water contained in the portable, pressurized unit to freeze. A co-worker then helped the employee remove his protective clothing and escorted him to the command post. There, a handheld eye wash station was used to irrigate the affected eye, and arrangements were made to take the employee to the hospital.

The employee's eye was thoroughly irrigated with eye solution at the hospital and he was released later in the day. He returned to work two days later after a thorough examination by an eye doctor indicated that no permanent damage resulted from the incident.

Case History #3

The third case illustrates the need to be aware of standard safety protocols for the specific rig in use, and emphasizes the severity of potential accidents surrounding a drill rig.

An air rotary drill rig was in-use at this site, which was being investigated under a Superfund RI program. Air rotary drilling methods involve the use of pressurized air which when forced down into a drill rod, turn a series of "toothed" drill bits. Air rotary techniques are extremely useful in hard rock formations. Twenty-foot (20) lengths of steel casing are used as a conduit for the drill cuttings and keeps the hole open as the bit is advanced downward. After the drilling reaches total depth, the well is constructed inside the casing, and the casing is removed in equal increments. When the well is constructed and after the bentonite and grout sets, the casing is pulled up using winches or hydraulics mounted on the mast of the rig.

Work at the site started in March and was scheduled to end in late April based upon 10-hour work days and six day weeks. At the time of the accident, the crew was behind schedule by 3 weeks due to weather conditions (rain, cold), and equipment failure. The drill rig in use was repeatedly experiencing breakdowns.

On the day of the accident, the crew had been at work at the same well location for 3 days. It was a deep well (85 feet) and progress had been slowed by a rig breakdown the day before. After reaching maximum depth, the crew commenced construction of the well and removal of the steel casing. The last 30 feet of casing got stuck in the hole. If it couldn't be removed, the well would have to be abandoned and a new well would have to be drilled. Without the 30 feet of casing that was stuck, a new well couldn't be started until replacement casing arrived on-site.

After several attempts to remove the stuck casing using the winches on the rig failed, the rig tender vehicle was positioned to take advantage of an additional crane. The rig tender is a flat bed truck equipped with water storage and a 2 ton crane. A towing chain, retrieved from the rig tenders tool box was wrapped around the casing and attached to the tenders crane. The idea was to use the crane in conjunction with the winches on the rig to forcefully remove the casing. The driller was located at the rig operator's station, the drillers helper was operating the crane, and a laborer was located at the back of the rig, opposite side of the rig operators station. The rig tender was perpendicular to the rig, and the crane was located over the laborer's position.

The removal operation was attempted twice without success using the rig tender crane. On the third attempt, the chain connected to the casing and the tender crane experienced a failed link. The failure occurred at the wrap of chain around the casing. The remaining 10+ feet of chain "snapped" towards the crane and hit the laborer in the mouth/chin area.

The crane operator was "grazed" in the head, but his hard hat deflected the impact.

The laborer suffered damage to his front teeth and a broken jaw. Following a visit to the hospital's emergency room, he was released later in the day and returned to work a week later.

Case History #4

This case illustrates the extreme potential of drill rig accidents and emphasizes the need to ensure that all site personnel receive training on rig specific emergency procedures.

The objective of the drilling operation was to determine the extent of contamination at a site located in Worcester, MA. A hollow stem auger rig was in use. The accident occurred on the second day of drilling for the crew, some of whom had never operated the specific rig in use. The accident occurred in June.

At the time of the accident, auger flights had been drilled into the hole, and were prevented from slipping by a "U" shaped collar device placed around the auger at ground level. The collar device had a "T" shaped handle which extended 3-feet upward at an angle from the "U." The collar is used to support the augers during the split spoon sampling operation. Following completion of sampling, the split spoon is retrieved, another auger flight is attached, the collar is removed, and the auger flights are turned by engaging the drive mechanism. The augers drill downward until the top of the top flight is 2-3 feet from ground surface. The collar is then used to secure the augers from slipping, and the split spoon sampler is inserted.

In this case, the driller failed to remove the collar before engaging the drive mechanism. As the augers turned, the collar and "T" handle also turned. The turning "T" handle apparently swept the driller from behind and pushed him into the turning auger flight(s). No other crew members were in the immediate area at the time of the incident. The auger flights turn at a speed of 1.5 revolutions per second. The inspection performed by the Occupational Safety and Health Administration (OSHA) revealed that several members of the crew responded to the accident, and the rig was de-powered by pressing the kill button. One crew member, however, approached the drill rig but didn't know how to shut it off.

The driller was taken to a hospital emergency trauma room where he later died of massive internal and external injuries. Police reports indicated that the driller was thrashed several times against the back of the rig. OSHA cited the driller's employer for failure to provide adequate training to the crew members on the hazards of the work area. OSHA also noted the employer's failure to ensure that all crew members were trained in the rig specific emergency procedures such as the location of shut off buttons. Additionally, OSHA cited the employer for alteration of the rig manufactures kill switches. The original switches were mushroom shaped but had a tendency to catch on personnel's clothing according to the employer. The mushroom shaped button was converted to a flush mounted push button. OSHA maintained that the reduced size of the button made it more difficult to see and utilize.

CONCLUSIONS

The authors hope you will agree that drilling operations at Hazardous Waste sites are more dangerous than normal drilling operations and do warrant additional health and safety training. OSHA now mandates various levels of specific training be given to all employees prior to assignment to hazardous waste operations. Hazardous waste drillers need to know at a minimum, about respiratory protection, protective clothing, site activities, air monitoring, medical monitoring, health and safety programs, chemical risks/hazards, site control, contingency planning/emergency response planning and last but not least engineering controls. In addition, site specific training should emphasize both the chemical and physical hazards on-site, and details of contingency or emergency plans implemented for the operation.

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Springfield, MA
Area Office
August, 1987

TEXAS AIR CONTROL BOARD PROGRAM TO MONITOR AIR TOXICS DURING SPILL RESPONSE

James P. Barta, Jr., P.E.
Texas Air Control Board

INTRODUCTION

The Texas Air Control Board (TACB) is the state agency legislated to protect the air resources of the State of Texas. To control the release of chemicals into the atmosphere, the staff is organized into various programs and divisions, ranging from enforcement, permits, research, and monitoring. The Monitoring Program is responsible for conducting all air monitoring for the the State. Within the Monitoring Program is the Sampling and Analysis Division which is responsible for all air testing and analysis. The Air Toxics Response Program (ATRP) works out of the Source Sampling Section with additional team members volunteering from areas within the Monitoring Program.

The TACB is a member of the State Emergency Management Council (SEMC), and as such, performs a major supporting role during spill response. This role has been as a coordinating and technical information network on air toxics. Only recently has a program been developed to safely monitor air releases during spill responses. Starting in 1985, the staff anticipated the need for having an emergency air response capability and began development of this program. The design and fabrication of the response vehicle, the procurement of dedicated equipment, and the training of the response staff has been completed and the program became effective January, 1989. The remainder of this paper describes the program developed to monitor air toxics during emergency releases.

AIR TOXICS RESPONSE PROGRAM

The program that has been developed combines trained staff using dedicated equipment. Responses are made through the agency's Emergency Management Center working in cooperation with the state-wide SEMC. There are limits to the types of responses which can be handled. Currently only one response vehicle is based in Austin. Therefore, the spill has to be of longer duration to allow the necessary driving time. Additionally, no responses are made to spills involving radiation or biological hazards since these types of spills are the responsibilities of other agencies. The primary function of the ATRP is to assist the on-scene coordinator by monitoring air releases in vicinities of impacted neighborhoods and to assess the health impacts. At the discretion of the team leader, other assistance may be provided as long as the primary objective is met. The ATRP staff has developed its operational guidelines[1] based upon guidelines published by the United States Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration[2,3,4].

Personnel

The staffing of the ATRP currently exists of a core unit with assistance from individuals volunteering from within the Monitoring Program. The Source Sampling Section staff comprises the core unit which performs the emergency response actions in addition to their regular source testing duties. The core response members serve as team leaders during response operations. The volunteers are chemists and environmental health specialists that assist in performing the tasks during responses. Currently, fourteen individuals are actively involved on the response team. The response team members average in excess of 10 years experience in the fields of sampling and analysis.

Additionally, the response team has been trained in response operations. This training is a combination of formal training courses and in-house drills and exercises. Table 1 lists the formal courses attended. All team members have taken a course in basic response operations with the core team members taking additional training in risk assessment and hazard recognition.

Courses Completed by ATRP Personnel

- Personnel Protection and Safety (EPA)
- Air Pollution Control Technology (EPA)
- Air Surveillance at Haz Mat Incidents (EPA)
- Air Toxics Workshop (EPA)
- Environmental Risk Assessment (EPA)
- Sampling For Hazardous Materials (EPA)
- Haz Mat First Responders Course (EPA)
- Emergency Medical Technician (ACC)
- Emergency Care Attendant (ACC)

TABLE 1.

The core team is responsible for the in-house training of the response team. Standard operating procedures have been developed and updated in the use of the specialized equipment. Routine drills are conducted using the equipment to maintain proficiency. Simulated response exercises are conducted quarterly when no actual responses have occurred in the preceding quarter.

Finally, the ATRP members participate in a medical monitoring program. This program allows for an initial medical physical to confirm individuals' capability to perform duties and annual physicals to document any exposures to toxic compounds. A summary of the medical tests are listed below.

* Personal / family history
* Previous work history
* Standard physical examination

* Pulmonary function screening test including:
  - forced vital capacity (FVC)
  - forced expiratory volume in 1 second (FEV)
* 14" x 17" posterior-anterior chest X-ray
* Electrocardiogram (EKG)
* Routine urinalysis
* Complete blood count (CBC)
* SMAC profile including:
  - sodium
  - glucose
  - SGOT
  - total protein
  - total cholesterol
  - potassium
  - uric acid
  - chloride
  - urea nitrogen
  - triglycerides
* Audiogram

Equipment

The equipment for use in air toxics response must remain in a state of readiness. To achieve this, the equipment is dedicated and housed in a self-contained forty foot trailer (Figure 1), complete with electrical generators and decontamination facilities. Additional features include a weather monitoring system, tanks for clean and waste water, analytical instruments, personnel protection gear, and CAMEO II chemical database with a plume dispersion modeling program. The trailer is towed with a two-ton, gasoline powered, flat bed truck having a dual speed rear axle.

Because of high costs and limited space, the response team has only the equipment necessary to perform its mission. In general, the equipment is not available for loan to other responders. The core team maintains and calibrates the equipment, and ensures consumable supplies remain fully stocked. A breakdown of the equipment is summarized in the following tables.

Sampling Equipment

- OVA 128 Organic Vapor Analyzer FID
- Alpha -1 pumps
- LEL Combustible Gas Monitors
- Geiger Counter
- Photovac PID
- Vacuum Pump with Colormetric Tubes
- Real Time Detectors :
  - * Ammonia
  - * Chlorine
  - * Hydrogen Chloride
  - * Hydrogen Fluoride
  - * Hydrogen Cyanide
  - * Hydrogen Sulfide

TABLE 2.

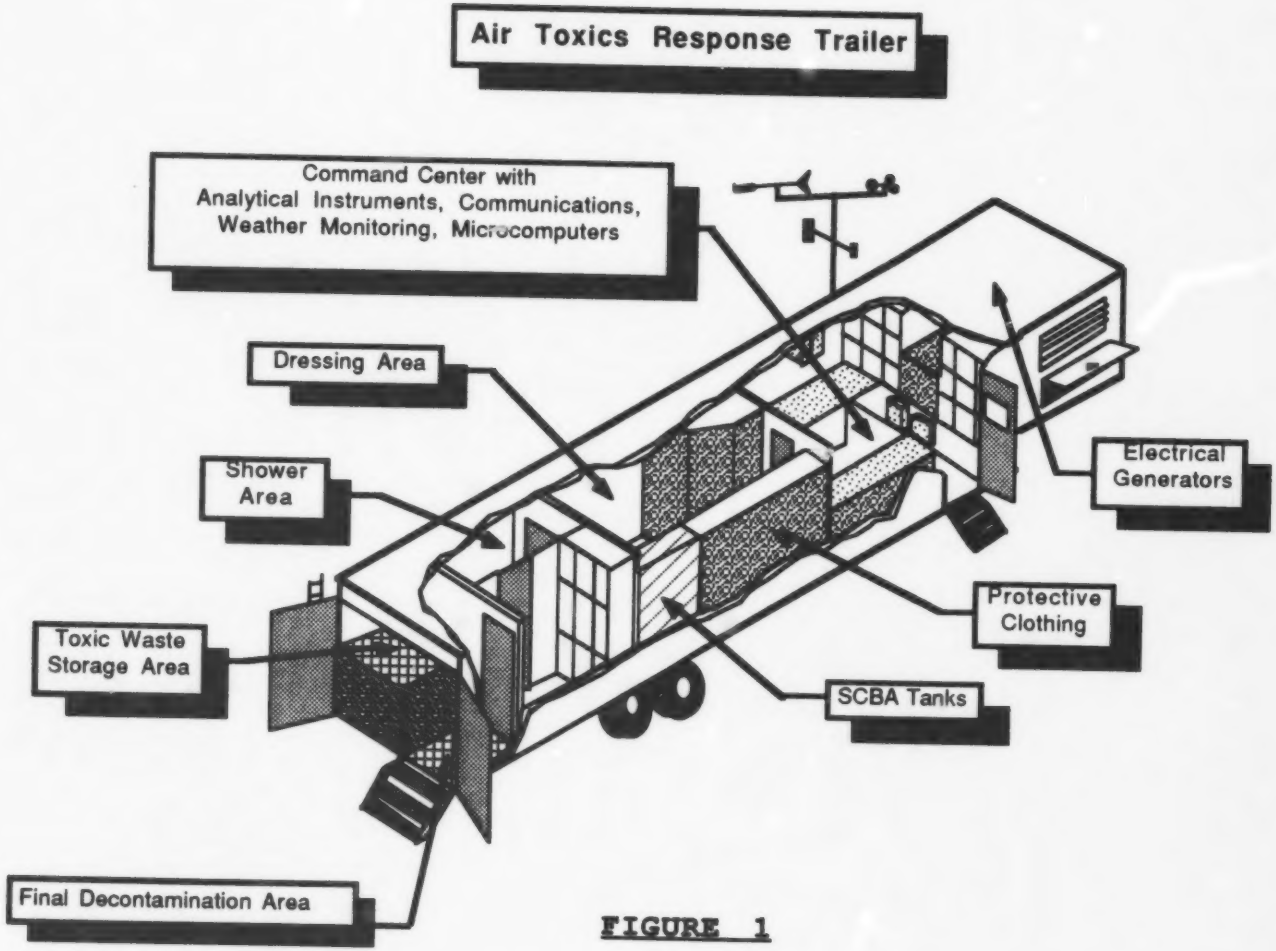
Air Toxics Response Trailer
Command Center with
Analytical Instruments, Communications,
Weather Monitoring, Microcomputers
Dressing Area
Shower
Area
Toxic Waste
Storage Area
Final Decontamination Area
Electrical
Generators
Protective
Clothing
SCBA Tanks

FIGURE 1

The sampling equipment can be used for survey instruments and for taking real-time measurements. The OVA 128 and the Photovac instruments measure total organics. The Alpha -1 pumps are programmable, battery-powered, constant volume pumps for collecting samples onto sample tubes. The response team uses a Sensidyne syringe type vacuum pump to draw samples into the colormetric tubes. Currently, the response team can detect approximately sixty compounds using the colormetric tubes. The combustible gas monitors Industrial Scientific Model LD222. The Geiger counter is a Technical Associates PUG-1. The real time detectors are Sensidyne SS2200.

Analytical Equipment
- Gas Chromatograph / Ion Trap detector with IBM computer data system and reference library

TABLE 3.

The gas chromatograph is a Varian Model 3400 which separates the sample into individual compounds. The Finnigan ion trap detector then can identify each separated compound by comparison of the fragmentation pattern to a reference library of compounds. Samples are prepared using both thermal and solvent desorption techniques.

Personnel Protection Equipment
- 7 SCBA with 22, one-hour air tanks
- Fully encapsulating disposable safety suits (Level A)
- Disposable splash suits (Level B)
- Full and half face respirators

TABLE 4.

Personnel protection and safety are the foremost concern of the response team. Different suit materials are stocked to allow the response team to meet the needs of the particular response. These materials include tyvek, saranex, and polyethylene. Decontamination facilities include a high pressure sprayer and showers. Separate holding tanks for toxics are built into the trailer with provisions for transfer to drums for proper disposal.

Communication Equipment

- Cellular Phone and Mobile Telephones
- Motorola Base Radio Unit
- 3, five-watt walkie-talkies
- 3, three-watt walkie-talkies with ear microphones
- Pagers for all members of the ATRP, with the core members on call 7 days a week, 24 hours a day.

TABLE 5.

Communications is a major part of the spill response. Effective and timely communications are required between team leader and the field crew of the response team, between the team leader and the on-scene coordinator, and between the team leader and technical assistance at headquarters, chemical manufacturer associations, or the transportation industry. Currently, the response program has two-way radio communication to the field crew, and telephone communication. Pagers are used to provide prompt mobilization. Plans are currently underway to provide a modem link-up to allow data transfer via the mobile telephones.

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DEVELOPMENT OF RAPID ANALYTICAL SYSTEMS FOR SPILL RESPONSE

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Since 1980, the Environmental Emergencies Technology Division of Environment Canada has had on-going projects to develop analytical systems for spill response. Research has focused on systems which can be used for the analysis of chemicals from Environment Canada's spill priority list. The selected systems are person-portable ones for on-site quantitative analysis of air, water and soil and vehicle portable analytical ones for quantitative and qualitative analysis. Reviews of the work done from 1980 to 1988 have been presented at several of the past Technical Seminar on Chemical Spills (Streutker, 1988; Goldthorp, 1988; Mills and Bobra, 1987; Ruttan, 1987; Bobra, 1986; Townshend-Colford, 1986; Underdown and Colford, 1985; Bobra, 1985; Lockwood and Halman, 1983a and b). This paper summarizes the work that has been done since the 1988 Technical Seminar on Chemical Spill presentation.

PERSON-PORTABLE ANALYTICAL SYSTEM

Work on the person portable analytical system has dealt with 2 areas: first, continuing development of a person-portable analytical kit (PPAK) and second, surveying and evaluating of available equipment. Each will be summarized briefly in the following section.

A) Person-Portable Analytical Kit (PPAK)

Work has been continuing on a Person Portable Analytical Kit for on-site analysis of chemicals in soil and/or water in which a single known chemical is involved. The existing system uses colorimetric and titrimetric techniques. The present kit can quantify approximately 70 chemicals from the priority list in water and 60 in soil. The kit also has the capability for quantitative testing of approximately 85 non-priority chemicals in water. Examples of chemicals which can be analyzed using this kit are given in Table 1. Information required for the

determination of concentrations of environmental contaminants with the kit is detailed in Environment Canada Report EE-110 (Goldthorp et al., 1989). An example of a typical entry, which has been written in the format of a user friendly manual for spill responders, is given in Table 2.

B) Survey/Evaluation of Portable Instrumentation for Field Use

A survey has been done of available person-portable analytical systems which are field worthy and provide quantitative results for a number of chemicals from Environment Canada's spill priority listing. The inclusion of instruments which satisfy the aforementioned criteria is based solely on information supplied by the manufacturers and distributors.

The information obtained for each instrument or series of instruments, includes the full address of both the manufacturer and the Canadian distributor (if one exists), the name of the instrument and the detection method employed. Also included is a description of the instrument such as display characteristics, alarms, detection levels, response time, accuracy, operating conditions, power requirements and ranges for detectable compounds. The physical dimensions of weight and size as well as the price in Canadian dollars follow the instrument description. An example of the format used is shown in Table 3. The survey will be published in the near future as an Environment Canada Report (Goldthorp, 1989).

In the survey, the listings are alphabetical with respect to the name of the manufacturing company. Charts which provide for easy cross referencing are also included in the review. An example of one of the charts (a portion only) is given in Table 4. This chart allows the user to select a compound (listed alphabetically) and determine which instruments can be used for quantitative analysis. Charts are also available for selection of instrumentation using a specific analytical technique or for use when chemicals are found in different environmental media (namely air, water and soil).

As stated earlier, all the information in this survey is supplied by the manufacturers and distributors. An evaluation program for instrumentation listed in this survey has been designed. It evaluates instruments in the following areas:

- -portability
- -rapidity
- -accuracy
- -sensitivity
- -simplicity of use, especially when wearing protective clothing (e.g. gloves, full face shield, etc.)
- -simplicity of maintenance
- -adaptability for use over a wide range of climatic conditions (e.g. temperature, humidity, etc.).

The evaluation program will commence in the near future on

selected instruments from the survey.

VEHICLE PORTABLE ANALYTICAL SYSTEM

This year, work on the vehicle portable analytical system has dealt with the continuing development of a vehicle portable analytical system and with surveying of methodologies which have a potential for use in the vehicle portable system. Each will be summarized briefly in the following section.

A) Vehicle Portable Analytical System

Work has been continuing on a Vehicle Portable Analytical System for on-site analysis of chemicals in air, soil, water and/or on various surfaces in which a single (known or unknown) chemical or a mixture of chemicals is involved. The existing system uses gas chromatographic (GC) techniques with photoionization, flame ionization and electron capture detectors. Basically the system has remained the same, as in previous years, with a few minor changes. These changes have included the installation of high temperature gas switching valves so that the two columns used can remain simultaneously installed, the changing of the computer search program from Fortran to C language to decrease the time involved in the search, additional methodologies for air and soil analysis and changes in the chemicals used for calibration. A more detailed description is provided by Vandenberg (1989a). The library system has been expanded to quantify and qualify approximately 70 chemicals by direct injection and 50 by headspace.

In addition to the continuing development work, the system was used at the site of the St. Basile-le-Grande polychlorinated biphenyl fire for the analysis of PCBs from wipe samples taken from various surfaces, and from soil and water samples. The rapid, on-site results from this system aided spill responders in their decision making process.

Plans are underway to update the present system by replacing the GC with a GC/MS and using various techniques, possibly supercritical chromatography, for sample preparation and extraction.

B) Survey of Analytical Methods for Pollutants in Air, Water and Soil

A survey of analytical chemical methods which can be used in the vehicle portable analytical systems for the quantitative analysis of chemicals in various environmental media, has been done (Vandenberg, 1989b). The survey is presented in a manual which is divided into three volumes with 410 analytical methods included. Volume 1 is a summary of Volumes 2 and 3. The first volume contains the indices for all the methods and a short summary of each method including such information as the procedure, the range and precision, the source and the environmental media to which the method is applied. An example

is shown in Table 5. Volume 2 contains the more detailed 135 methods for the analysis of chemicals in air. Volume 3 contains 170 methods for the analysis of chemicals in water and 105 methods for the analysis of chemicals in soil, also included are the sample collections and extraction technique methods.

This paper provides a brief review of the work that has continued on the vehicle and person portable analytical systems for the period of 1988 to the present time. Both of these systems give a high degree of coverage for the priority list chemicals. They have developed, and are being further developed, into valuable and essential components of a comprehensive chemical spill response capability.

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TABLE 1

EXAMPLES OF CHEMICALS WHICH CAN BE ANALYZED USING THE PERSON PORTABLE ANALYTICAL KIT

in water-

ANALYTE	RANGE (mg/L)	TYPE OF TEST
Acetic Acid	0-10000	Titrimetric
Acetic Anhydride	10-2000	Titrimetric
Acetone	0-400	Colorimetric
Acrylonitrile	100-2000	Titrimetric
Adipic Acid	0-10000	Titrimetric
Aluminum Chloride	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric
Ammonium Chloride	0-25000	Titrimetric
Ammonium Nitrate	0-80	Colorimetric
Ammonium Phosphate-		
Dibasic	0-30	Colorimetric
Monobasic	0-25	Colorimetric
Benzene	0-15000	Colorimetric
Benzoic Acid	0-10000	Titrimetric
1-Butanol	200-8000	Colorimetric
iso-Butyraldehyde	0-40	Colorimetric
n-Butyraldehyde	0-40	Colorimetric
Calcium Chloride	0-25000	Titrimetric
-Monohydrate	0-25000	Titrimetric
-Dihydrate	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric
Calcium Hydroxide	0-10000	Titrimetric
Calcium Oxide	0-10000	Titrimetric
Calcium Phosphate	0-25	Colorimetric
*Carbon Dioxide	0-1000	Titrimetric
*Chlorine, Free	0-2	Colorimetric
*Chlorine, Total	0-2	Titrimetric
Cumene	0-15000	Colorimetric
Ethanol	200-10000	Colorimetric
Ethanolamine	0-500	Titrimetric
Ethylbenzene	0-750	Colorimetric
Ethylene Glycol	0-500	Titrimetric
Ferric Chloride	0-25000	Titrimetric
-2.5 Hydrate	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric
Formic Acid	0-10000	Titrimetric
Hydrochloric Acid	0-25000	Titrimetric
Hydrochloric Acid	0-10000	Titrimetric
Hydrogen Peroxide	0-10	Colorimetric
Hydrogen Peroxide	0-75	Titrimetric
Isopropanol	200-10000	Colorimetric
Maleic Anhydride	25-1000	Titrimetric
*Mercury	0-100	Colorimetric
Methyl Ethyl Ketone	0-400	Colorimetric
Methanol	500-10000	Colorimetric
MIBK	0-400	Colorimetric
Morpholine	100-2000	Titrimetric

Nitric Acid	0-10000	Titrimetric
NTA	40-1500	Titrimetric
*Phenol	0-0.2	Colorimetric
Phosphoric Acid	0-15	Colorimetric
Phosphoric Acid	0-10000	Titrimetric
*Phosphorus	0-20	Colorimetric
Potassium Chloride	0-25000	Titrimetric
Potassium Hydroxide	0-10000	Titrimetric
Propylene Glycol	0-500	Titrimetric
Sodium Carbonate	0-10000	Titrimetric
Sodium Chloride	0-25000	Titrimetric
Sodium Hydroxide	0-10000	Titrimetric
Sodium Phosphates	0-70	Colorimetric
Sulfuric Acid	0-10000	Titrimetric
Toluene	0-2500	Colorimetric
Urea	0-200	Colorimetric
o-Xylene	0-1500	Colorimetric
m-Xylene	0-1000	Colorimetric
p-Xylene	0-1500	Colorimetric
Zinc Chloride	0-25000	Titrimetric

* designates those tests which were already included in the HACH kit.

in soil-

ANALYTE	RANGE (mg/kg)	TYPE OF TEST
Acetic Anhydride	500-5000	Titrimetric
Acrylonitrile	500-4000	Titrimetric
Adipic Acid	200-4000	Titrimetric
Aluminum Chloride	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric
Aluminum Sulfate	0-25000	Titrimetric
-18 Hydrate	0-25000	Titrimetric
Ammonium Chloride	0-25000	Titrimetric
Ammonium Nitrate	100-4000	Colorimetric
Ammonium Sulfate	0-25000	Titrimetric
Benzene	0-15000	Colorimetric
Boric Acid	500-5000	Titrimetric
1-Butanol	2000-40000	Colorimetric
iso-Butyraldehyde	0-150	Colorimetric
n-Butyraldehyde	0-200	Colorimetric
Calcium Chloride	0-25000	Titrimetric
-Monohydrate	0-25000	Titrimetric
-Dihydrate	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric
Cumene	0-15000	Colorimetric
Ethanol	2000-35000	Colorimetric
Ethylbenzene	0-10000	Colorimetric
Ethylene Glycol	100-3000	Titrimetric
Ferric Chloride	0-25000	Titrimetric
-2.5 Hydrate	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric

Hydrochloric Acid	0-25000	Titrimetric
Isopropanol	2000-50000	Colorimetric
Maleic Anhydride	250-5000	Titrimetric
Methyl Ethyl Ketone	0-500	Colorimetric
Methanol	2000-40000	Colorimetric
MIBK	0-500	Colorimetric
Morpholine	500-5000	Titrimetric
NTA	250-5000	Titrimetric
Phthalic Anhydride	200-4000	Titrimetric
Potassium Chloride	0-25000	Titrimetric
Potassium Sulfate	0-25000	Titrimetric
Propylene Glycol	150-3000	Titrimetric
Sodium Chloride	0-25000	Titrimetric
Sodium Sulfate	0-25000	Titrimetric
-Heptahydrate	0-25000	Titrimetric
-Decahydrate	0-25000	Titrimetric
p-Terphenyl	0-15000	Colorimetric
Toluene	0-10000	Colorimetric
Urea	0-4500	Colorimetric
Vinyl Acetate	250-3000	Titrimetric
o-Xylene	0-6000	Colorimetric
m-Xylene	0-7000	Colorimetric
p-Xylene	0-6000	Colorimetric
Zinc Chloride	0-25000	Titrimetric
Zinc Sulfate	0-25000	Titrimetric
-Hexahydrate	0-25000	Titrimetric
-Heptahydrate	0-25000	Titrimetric

TABLE 2

AN EXAMPLE FROM THE MANUAL FOR THE PERSON PORTABLE ANALYTICAL KIT

ACETONE IN SOIL

2,4-DINITROPHENYLHYDRAZINE METHOD

Reference: Critchfield, F.E., Organic Functional Group Analysis, Permagon Press, 1963.

Range: 0 - 1200 mg/kg

Common Synonyms: Dimethylketone, 2-Propanone, Methyl Ketone

HAZARDOUS DATA

Human Health
Symptoms: Contact - skin- slight reddening and dryness; eyes- redness and irritation. Inhalation - coughing, headache, nausea, dizziness, narcosis. Ingestion - sore throat, headache, dizziness, narcosis, coma.
Toxicology: Only slightly toxic upon contact, inhalation and ingestion.
TLV - 750 ppm; 1780 mg/cubic meter
Short-term Inhalation Limits - 1000 ppm; 2375 mg/cubic meter

Environment: Prevent entry into waterways and intakes. Harmful to aquatic life. Fish toxicity: 14250 ppm/24h/sunfish/killed /tapwater; BOD: 38 to 81 %, 5 days.

EXPERIMENTAL REQUIREMENTS

Apparatus: Hach Spectrophotometer and 2 cuvettes
2 x 100 mL Graduated Cylinders
2 x 250 mL Erlenmeyer Flasks
2 x 100 mL Mixing Cylinders
5 x 10 mL Disposable Pipets
2 x 150 mL Beakers
1 x 100 mL Volumetric Flask
Timing Device
Whatman #1 Filter Paper
2 x Long Stemmed Funnels
Balance

REQUIRED REAGENTS

Pyridine Stabilizer
33% Potassium Hydroxide Solution
2,4-Dinitrophenylhydrazine Solution

Preparation of Pyridine Stabilizer

Add 100 mL of deionized water to 400 mL of pyridine. Mix thoroughly. Store in a brown glass bottle.

Preparation of 33% Potassium Hydroxide Solution

Dissolve 33.0 g of potassium hydroxide in a 150 mL beaker containing 100 mL of methanol.

Preparation of 2,4-Dinitrophenylhydrazine solution

Dissolve 0.100 g of 2,4-Dinitrophenylhydrazine in a 100 mL beaker containing 50 mL of methanol and 4 mL of concentrated hydrochloric acid. Transfer the solution to a 100 mL volumetric flask and dilute to the 100 mL mark with deionized water.

PROCEDURE

1. Weigh into a clean 250 mL Erlenmeyer flask 10 grams of soil from an uncontaminated area. Label the flask BLANK.

2. Weigh into a second clean Erlenmeyer flask 10 grams of soil from the contaminated area of interest. Label the flask TEST.

3. Using a graduated cylinder, transfer 100 mL of water to each flask. Mix well.

4. Filter the contents of each flask through Whatman #1 filter paper into separate, clean 150 mL beakers. Label the beakers to match the originating flask.

5. Transfer 50 mL of each filtrate into separate mixing cylinders.

6. Pipet 1.0 mL of the 2,4-Dinitrophenylhydrazine solution into each mixing cylinder. Stopper and shake gently. Wait exactly 20 minutes.

7. Pipet 1.0 mL of the 33% potassium hydroxide solution into eacn mixing cylinder. Then add 5 mL of pyridine stabilizer to each and stopper. Mix well and wait 2 minutes for colour stabilization.

8. Adjust the Wavelength Dial of the spectrophotometer to read 480 nm.

9. Insert the Zero Scale card into the card holder of the spectrophotometer. Hold the toggle switch to Zero Check and adjust the Zero Adjust Dial until the needle position corresponds

to the zero mark on the card.

10. Replace the Zero Scale card with the ACETONE in SOIL card.

11. Fill one cuvette to the 25 mL mark from the cylinder labelled BLANK. Insert this cuvette into the sample holder of the spectrophotometer and close the lid.

12. Turn the toggle switch to ON. Turn the Light Control Dial until the needle position corresponds to the zero mark on the card. Turn the switch to OFF and remove the sample.

13. Fill the other cuvette to the 25 mL mark from the cylinder labelled TEST. Insert this cuvette into the sample holder and close the lid. Turn the toggle switch to ON. Read the acetone concentration from the card and record this result.

TABLE 3

AN EXAMPLE FROM THE REVIEW OF PORTABLE INSTRUMENTATION FOR FIELD USE

MANUFACTURER:

The Foxboro Company
Foxboro, MA. 02035
USA

DISTRIBUTOR:

Nortech Control Equipment, Inc
135-4 The West Mall,
Etobicoke, Ontario.
M9C 1C2

MODEL NAME:

Century OVA 128 Portable Organic Vapor Analyzer

DETECTION METHOD:

Flame Ionization

MODEL DESCRIPTION:

This is a dual mode analyzer. For instantaneous levels of hydrocarbons (calibrated to methane) the survey mode can be used, where the sample gas is pumped directly to the flame ionization chamber for combustion and analysis within 2 seconds. This model also contains a built-in chromatographic column. For identification of gases, the sample is injected onto the packed column and the retention time is monitored. The peaks are shown on the analog scale on the probe as they elute from the column, but for more accurate results, an optional chart recorder can be added. Once the specific gas is known, a meter scale overlay will calibrate the instrument to the specific gas range. The range for methane is 0 to 10, 0 to 100, or 0 to 1000 ppm, depending on the scale desired.

The flame is fueled by an internal compressed hydrogen tank. If the flame is extinguished, visual and audio alarms are triggered. The unit is powered by a 12 V rechargeable battery for a minimum of 8 hours of use. The probe can be extended 1.2 m from the body of the instrument. The unit comes complete with case, tool kit, probes, 2 chromatographic columns, charcoal filter, battery charger, manual and accessories.

UNIT SIZE: 23 cm x 30 cm x 10 cm

UNIT WEIGHT: 5.5 kg

UNIT COST: $ 9905.

for Tri-column option (for Benzene analysis) including a stripper column and T-24 column -
$ 10590.

TABLE 4

EXAMPLE OF A CHART FOR EASY CROSS REFERENCING FROM THE SURVEY OF PORTABLE INSTRUMENTATION FOR FIELD USE (ONLY A SMALL PORTION IS SHOWN OF THE COMPLETE CHART)

COMPOUND	MANUFACTURER	MODEL NAME	METHOD	MEDIA
All priority list gases	Enmet	Toxic Gas Detector kit	COL	A
All priority list gases	Foxboro	Miran 1A	IR	A
All priority list gases	Foxboro	Miran 1B	IR	A
All priority list gases	Foxboro	Miran 101	IR	A
All priority list gases	Foxboro	Miran 103	IR	A
All priority list gases	Gastec	Detector tubes	COL	A
All priority list gases	HNU	Model 311	GC	A,W
All priority list gases	IST	AG5000	SS	A
All priority list gases	IST	AG5100	SS	A
All priority list gases	Microsensor	M200	GC	A
All priority list gases	MSA	Samplair kit	COL	A
All priority list gases	National Draeger	Detector tubes	COL	A
All priority list gases	Sensidyne	HazMat kit	COL	A
All priority list gases	Sentex	Scentograph	GC	A,W
All priority list gases	Sentex	Scentor	GC	A,W
All priority list gases	SKC	Color-detector tubes	COL	A
All priority list gases	Summit Interests	SIP-1000	PI,FI,TC	A
All priority list gases	Thermo	Model A511	GC	A,W
All priority list gases	Thermo	Model A210	GC	A,W
All priority list gases	Xontech	GC-810 .	GC	A,W
Acetic Acid	HNU	HW-101, PI-101, GP-101	PI	A
Acetic Acid	Photovac	TIP	PI	A
Acetic Acid	Thermo	OVM 580A	PI	A
Acetic Acid	Thermo	OVM/GC 590	PI, GC	A,W
Acetic Anhydride	HNU	HW-101, PI-101, GP-101	PI	A
Alconols	Foxboro	OVA 128	FI	A
Alconols	Foxboro	OVA 108	FI	A
Alconols	Foxboro	OVA 98	FI	A
Alconols	HNU	HW-101, PI-101, GP-101	PI	A
Alconcis	Photovac	Photovac 10S	GC	A,W
Alconols	Photovac	TIP	PI	A
Alconols	Thermo	OVM 580A	PI	A
Alconols	Thermo	Series 700	FI	A
Alconols	Thermo	OVM/GC 590	PI, GC	A,W
Aldenydes	HNU	HW-101, PI-101, GP-101	PI	A
Aldenydes	Photovac	Photovac 10S	GC	A,W
Aldenydes	Photovac	TIP	PI	A
Aldenydes	Thermo	OVM/GC 590	PI, GC	A,W
Aldenydes	Thermo	OVM 580A	PI	A
Aliphatic Hydrocarbons	Westinghouse	Hycrocarbon Sensor	SS	W
Amines	HNU	HW-101, PI-101, GP-101	PI	A
Amines	Photovac	TIP	PI	A
Amines	Thermo	OVM/GC 590	PI, GC	A,W
Amines	Thermo	OVM 580A	PI	A
Ammonia	CSA	TGM 555	COL	A
Ammonia	Chemetrics	System 1000	COL	W
Ammonia	Gastech	Gasfeector 47 .	EC	A
Ammonia	Hach	DREL/2000	COL,T	W
Ammonia	Hach	DREL/2000 (Soils)	COL,T	S

COL-colorimetric
IR -infrared dispersive
GC -gas chromatography
SS -semi-conductor sensor

PI -photoionization
FI -flame ionization
TC -thermal conductivity
EC -electron capture
T -titrimetric

A- air
W- water
S- soil

TABLE 5

Analytical Methods For Acetone in Air, Water and Soil

Analyte:	Acetone (AIR)
Procedure:	Adsorb on charcoal, desorb with carbon disulfide, determine with GC/FID
Range:	1200 - 4500 mg/m^3
Precision:	CV_T 8.2%
Source:	NIOSH; Manual of Analytical Methods, Vol.2 (1977), S1.

Analyte:	Acetone (1) (WATER)
Procedure:	Treat with 2,4-dinitrophenylhydrazine and potassium hydroxide, determine colorimetrically
Range:	0 - 400 mg/kg
Precision:	10%
Source:	Critchfield, F.E.; Organic Funtional Group Analysis, Permagon Press, New York, 1963.

Analyte:	Acetone (2)
Procedure:	Determine with direct aqueous injection/GC/FID. This paper gives Kovats indices for over 100 volatile organics.
Range:	MDQ ~1 mg/l
Precision:	Unknown
Source:	ASTM, Annual Book of ASTM Standards, Part 11: Water, 1982, Method D 3695 - 82.

Analyte:	Acetone (SOIL)
Procedure:	Treat with 2,4-dinitrophenylhydrazine and potassium hydroxide, determine colorimetrically
Range:	0 - 1200 mg/kg
Precision:	10%
Source:	Critchfield, F.E.; Organic Functional Group Analysis, Permagon Press, New York, 1963.

MDQ Minimum Detectable Quantity
CV_T Coefficient of Variation (Total)

HAZARDOUS MATERIALS IDENTIFICATION
A QUICK FIELD IDENTIFICATION OF UNKNOWN MATERIALS

Robert Turkington

ABSTRACT

The HazCat system uses forty-four one or two step field tests arranged into a decision tree format which allows a non-chemist to quickly key out an unknown material at the scene of an incident. With a few exceptions, the entire system is made up of equipment and reagents which can be stored for over a year in the trunk of a car and be immediately available for use.

BACKGROUND

California's Division of Occupational Safety and Health conducted a three-year study to look at the risk to emergency responders from exposure during fires and chemical spills. Hazardous Materials Identification was devised to provide for quick decisions on the part of Cal/OSHA Personnel who would be required to respond during the period of the study. This ability was deemed necessary after an ardous twelve hours on the San Francisco Bay Bridge which had been closed for a spill of unknown material (later determined to be talc). Initially, Hazardous Materials identification provided only enough information to stabilize a situation.

Other public agencies requested and were given training in the procedure. The training created a need for more refined tables as the users were made up of a broader spectrum of persons having varying degrees of chemical knowledge.

The number of requests increased until the class was being taught three times per week. Cal/OSHA recognized that there was a need for this type of training and decided to formalize the system. Formalization began by taking the list of one hundred and sixty of the most commonly spilled chemicals in the state of California, derived from the risk assessment study, and expanding the charts to include all of these for specific identification. Extremely hazardous materials not on the list but which could be a major hazard to a person using the system were added at this time. During this stage of development, each class was used as a research project. Students were encouraged to bring in unkowns that they had encountered. This provided Cal/OSHA a mechanism to test the validity of the system; it also tended to expand the charts quickly. Fine tuning of the system was done by modification based on student difficulty in reading the charts or performing the tests. Unknowns used in class instruction were constantly changed to ensure that all the theoretical pathways were attempted by persons new to the system. Questions from persons using HazCat in the field also resulted in numerous modifications. The charts as they are now presented are the end products of thousands of hours of hands-on testing by fire, police, health, and other response persons.

METHODOLOGY

Hazardous Materials Identification uses three tests to quickly separate an unknown liquid or solid into a unique universe. Two of these tests, the Water Solubility and Char tests are the key as they each divide materials into as many as one hundred distinct universes. After a mater-ial has passed through these two tests, it falls into an area where there remain very few possible candidates from among the more commonly encountered spilled materials. Once a mater-ial is in this realm, the devisive process is replaced by a searching process using positive identification methods to look look for common materials.

The third test is the Oxidizer test. Although this test defines only two possible universes, it quickly separates out some of the more hazardous materials. The oxidizer test is first.

The Oxidizer Test

The HazCat system uses potassium iodide paper. this test does not identify benzyol peroxide or nitrates. These are identified further into the system. This test is the first performed for two reasons: a. It is the first time an unknown is challenged with water. this challenge is perform-ed by moistening the potassium iodide paper with weak hydro-chloric acid and touching the unknown material, which is on an open flat watch dish. Even if the user was able to get sodium metal or other strong reactor to this point, the reaction would not harm the person performing the test. b. Oxidizers come in many chemical forms, and all are incompatible with other mater-ials. Since these very hazardous materials may not have many warning properties, it is best to know as soon as possible what has been spilled.

The Water Solubility Test

A small amount of the unknown is added to 10 ml of water is a test tube. There are more than 14 possible reactions when a material is placed in water. When this is considered in context with the more than 10 recongizable forms the unknown may take (e.g., viscosity for liquids, crystalline, metallic, waxy, etc., for solids), this test can separate unknowns into more than 100 unique universes. Many of these the layman is already familiar with from life experience. An example:

> Solvent-like material (no more viscous than water, but, has odor, separates from water, and/or is flammable) is placed in water; if it:
>
> a. Floats: it is most likely a petroleum hydrocarbon; secondary possiblities, plant distillate (turps) or long chain alcohols.
>
> b. Sinks: it is most likely a chlorinated cleaning solvent; secondary possibilities, freons and carbon disulfide. Hazards: more toxic than petroleum hydrocarbons; many have few warning properties; many are asphyxiants. If fire, the gases evolved may be very hazardous.

c. Dissolves: it is most likely an alcohol or acetone. Secondary possibilities, nitriles, short chain amines. Hazard: flammable. A slight possibility that the gases in a fire might be extremely toxic.

d. Emulsifies: it is most likely a pesticide, either chlorinated, thionated or organophosphate. Hazard: skin contact, extreme environmental hazard if the pesticide is chlorinated.

e. Reacts: most likely thynolchloride (commonly found in drug laboratories). Hazards: skin contact, may be explosive in many circumstances, is water reactive, probably acidic, and off-gasing material is also hazardous.

Oily material (viscous) is placed in water; if it:

a. Floats: it is most likely a petroleum hydrocarbon or plant distillate, also possibility of cooking (plant or animal oil). Hazard: flammable to combustible, depending upon how viscous the material appears (how it coats the side of the test tube). Primary concern--is this a carrier for some other product, PCBs, etc.?

b. Sinks: this is an area where some of the most hazardous materials are found; therefore, with oily things that sink, Hazardous Materials Identifications becomes very conservative. The most common spill is PCB which is the most likely candidate and therefore, the first thing that the system at looks for. If this is ruled out, then one has to consider the possibility of such chemicals as organo-metals and aniline. Hazard: if not PCBs, may be extreme skin contact poisons. Fire may produce extremely hazardous gases.

c. Dissolves: most likely, sugar solutions, or soap, however, one must consider long chain amines. Hazard: if the material has a very high pH, you may have an amine; these can be very hazardous both upon skin contact, and by inhalation. Sugar solutions, if found under suspicious circumstances, should be considered as possible baits.

d. Emulsifies: if very viscous, you may have a cutting oil, but before you can classify as such, you must rule out pesticides.

This process continues for liquids including pastes, goos, aqueous solutions and gels.

The Char Test

Take about 10 ml of the material, place it in a test tube and heat using a propane torch, continue to heat until no further change takes place in the

material being heated. For safety's sake, in Hazardous Materials Identification the Char Test has been broken into 3 tests. One has only to consider the results of placing 10 ml of a flammable liquid into a test tube and heating it to 1800· to understand. The second manifestation of the char test is called the Combustibility test. In this test, a small amount of a liquid is placed into a color plate, and a match is touched to the surface, if it is impossible to get the material to burn, then the more traditional char test may be done. The third test, Ignition, is unique in that it allows the person doing the test to use his/her creativity, to ignite the material any way they feel is possible. This test picks up such diverse materials as sulfur, magnesium, acetylene and hydrogen gases, and polyol solutions. The char test gives over 12 possible results, and in conjuction with the combustibility and ignition tests give 15 exclusive results placing the user into numerous possible universes. Initially the char test was the primary test, however for the sake of safety it was relegated to the secondary divisive test, where it is used mainly to distin-guish between organic and inorganic materials. The char test far more than the water solubility test gives very specific indications of what the unknown might be. In general, it identifies salts, oxides, silicates, and mixtures; more specifically, it identifies nitrates, ammonium salts, and arsenic salts.

Since so many hours of hands on time has been devoted to this system, and the changes since conception have been so great, by the time that a person arrives at the positive confirmation tests, the potential interferences have been largely eliminated. Highly technical persons may feel a faster method is available, as they pass through the series of tests, but the screening tests, and safety loops are based not upon the easiest method for achieving identification, but elimination of confusion and false positives for the uninitiated user.

Perhaps the most unique of these screening tests is the hexane/alcohol solubility test with its ability to pick out solid poisons such as pentachlorophenol, and parathion before these can get into the body of the system. Although these would eventually be found, this greatly shortcuts the process, and excludes many confusing results in the down stream positive tests.

Hazardous Materials Identification will not stop at a first identification or a Hazard category. Often it will force a user through two or three categories, before describing the material as; a water reactive acid, flammable peroxide, or carcin-ogenic oxidizer.

When a positive identification is finally made, previous tests become part of the confirmation. An example: The final test in the series keying out organophosphates uses the technique of killing cholinesterase enzymes. Prior to that final test, the user will have passed through the following observations:

1. Foul odor; 2. Emulsified in water; 3. pH was slightly acid; and 4. A confirmation of phosphate ion. If a person wishes to go further he can dd sodium hypochlorite. If it turns red, the unknown is methylparathion one of the more toxic of the organophospates commonly available.

If after all tests, the screening and safety loops the mater-ial is still unidentified, the user will still know the following:

a. Is the unknown material organic or inorganic? It is here that the Char test may be the most useful, in that, if the unknown is not volatile or reactive at 1800·, although it may remain an unknown, the responder can make the assumption that the material is not likely to be airborne and clean it up using the criteria for yanide.

b. The hazard category into which the material falls, (with the exception of toxic, which is always a good assumption).

An example: A fire department keyed out a material as unknown. By testing they knew it was aromatic, chlorinated, flammable, and acidic. When a laboratory analysis was finally available, the material turned out to be a mixture of toluene, perch-loroethylene, and formic acid. Although not specifically identified, the fire fighters knew how to handle the liquid.

The Hazardous Materials identification system incorporates 5 colorimetric paper strips, 7 dreager tubes, the EPA Asbestos ID system, Enztec orga-nophosphate test strips, the Chlor-n-oil test kit for PCBs, and salt solutions reagents, and specific indicater dyes. Except for some of the Dreager tubes, the reagents are very specific indicater dyes described in Fygle. Except for some of the Dreager tubes, the reagents are very stable.

The following example will show how the system works.

SECONDARY CONTAINMENT LINERS "AN OVERVIEW"

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I. INTRODUCTION

Environmental protection has become a major public and political concern in Canada and consequently an economic factor within the commercial sectors of industry. The "cradle to grave" approach, with regards to leaks or spills of prohibitive substances, is being considered for determination of the responsibility for a company.

Potential environmental damage and cost of clean ups are dictating the necessity for extra facility protection and secondary containment. One of these options that is available for use is the secondary containment geomembrane liner system.

This paper has been prepared to present the proper guidelines and procedures required to successfully design, fabricate and install an assured system.

II. MATERIAL SELECTION AND ENGINEERING CONSIDERATIONS

In all cases, the two most important considerations for the geomembrane liner applications are: 1) Material Compatibility and 2) Volumetric Considerations.

The choice of geomembrane material composition will be the ultimate determining factor in the successful containment of the fluid. The most important physical properties to consider are - degredation, permeability and volume swell, when the liner is in direct contact with the contained medium. In order to accurately test the liner compatibility, confirm the application with the material manufacturers or in the case where compatibility is unknown or questionable, arrange for containment/immersion tests to be performed by the manufacturers or independent laboratory. The minimum test duration shall be 30 days unless duration length is an expected necessity. In all cases obtain warranty for the subject liner only to the material manufacturer's specifications, guarantee,

and warranty containment capabilitiles within test parameters or your liability exposure will be compromised.

Permeability of a fluid through a geomembrane occurs by osmosis, diffusion and absorption. In most cases, this is expressed as oz./ft²/day for the vapor phase of the fluid. These values can only be arrived at through actual lab test procedures. Most material manufacturers supply these values on their test reports.

Some material manufacturers rate their geomembranes using the Darcy coefficient of permeability, "k", in cm/sec. Liners do not react the same as flow through a porous medium and consequently these "k" values are meaningless. They are only useful in comparing different liner applications to give apparent values only.

Calculations for penetration rates and volumes can be performed using the following formula.

$$Q = \frac{A\sqrt{H}}{80}$$

Q = max. permissible leakage rate thru liner - GAL/MIN.
A = lined area in 1000's sq. ft.
H = max. head of liquid in ft.
80 = conversion factor

To convert to "apparent" hydraulic flow, the following equations will apply.

V = ki
V = rate of seepage from lined area in velocity terms (i.e. cm/sec.)
k = apparent coefficient of permeability
i = hydraulic gradient

$$i = \frac{L}{L} = \frac{\text{head of fluid (ft, cm, m etc)}}{\text{liner thickness (in, mm, etc)}}$$

Q = kiA
Q = flow through liner in GAL/DAY, M^3/DAY etc.
A = lined area in FT^2 or M^2

The resulting values should be used as a guide only. Lined areas should, at a minimum, be able to achieve an apparent permeability of 1×10^{-7} cm/sec. At the present time, the best that could be expected is 1×10^{-10} cm/sec.

When selection of a proper liner is being made, site conditions and operational conditions must be properly evaluated. The conditions that must be addressed are as follows:

1) Soil conditions and liner buried depth
2) Maximum, minimum and average temperatures
3) Type of overburden
4) Exposure to sunlight/weathering
5) Installation and operating, loads on liner
6) Accessibility of site to "traffic"
7) Anchoring/sealing requirements

The foregoing conditions will dictate the physical properties that a geomembrane liner must have to provide the client with the

necessary assured containment service life. All geomembrane liners must be evaluated for their physical properties according to accepted testing standards. These standards are listed in table A according to liner type.

With respect to the design considerations for secondary containment liners, the volumetric calculations of the primary contained fluids will help determine the ultimate liner system design. For above ground secondary containment liner systems, the liner can either be sealed to an impervious dyke at ground level or designed to cover the complete area to the dyke crown. The contained volume in a complete lined system should equal the tank volume + maximum precipitation volume for a 24 hr period + safety factor of 10%.

Other considerations for above ground facilities include pump out/sump design for precipitation or spill pump off and if a protective backfill is placed on top of the surface liner, volumetric calculations for reduced containment volume must be carried out. The previous mentioned safety factor for lined volume can be assured as the tank will not empty completely even on a catastrophic failure. It will only empty to the equalized volume (height) that the containment area can hold.

Underground tanks can be lined in several ways. These include:

1) secondary liner to encompass each tank
2) secondary liner for complete buried facility
3) secondary liner for piping only (for double walled tanks)

Planned legislation dictates all liners must line the intended area to surface, contain sumps and monitoring stations and have an apparent permeability rate of less than 1×10^{-7} cm/sec. You should ensure all regulations are followed for installations and that the chosen geomembrane material meets or exceeds the required minimum permeabilities.

III. SECONDARY CONTAINMENT - SURFACE FACILITIES

A) SITE DESIGN AND PREPARATION

Once the construction plans have been drawn up for a facility, a few specific items must be addressed as it applies to the lined area. Ensure that the lined area contains a corner slope for liquid drainage to a pump out sump facility. Where possible, the piping should be designed for minimal liner breach. Ensure that proper elevation planning has been done for tank bases so that after the liner has been placed, elevation allowances are considered for placement of a 2 - 4" protection "pad" on top of the liner for tank placement. All volume calculations should be checked and final liner decision made based upon type of berms to be used.

Depending on fluid containment, the type of liner material may dictate the use of "skirts" to provide for extra U.V./weathering protection on exposed liner areas.

The site preparation plans will be dictated or will dictate the use of geotextile mechanical protection for the liner. All ground should be smooth, free of debris and most organic substances. Prior to a liner installation, the intended area sould be sprayed with an appropriate herbicide to prevent vegetation growth. The lined area should be well compacted (95% MODIFIED PROCTOR) and any unstable soil removed. In most existing facilities the existing ground compaction will be sufficient as the liner will not be under heavy continual loading.

Fabricate all liners to include a minimum of 2 - 10% oversize. The oversize is to allow for thermal expansion/contraction of the geomembrane as well as load settling allowance. The actual oversizing is dependent upon the type of liner to be used, unloaded liner lengths, temperature variations and conditions. Where possible, the liners should be prefabricated into as large a panel size

as possible to eliminate or reduce "non controlled" field seams. All liner seams should be fusion bonded to material manufacturer's specifications which will be dielectric, RF, heat or extrusion types of fusion depending on the geomembrane material. All seams, except for extrusion type on polyethylene, will be minimum 1½" wide for seam strength and assurance against failure.

All prefabricated panels should be pre-inspected for abrasion, flaws and competent seams. This inspection process will be visual and non destructive for the seams in combinations of alternatives.

In addition visual, non destructive, and destructive testing alternatives are available to confirm fusion seam competency. These tests include vacuum, forced air, peel, mechanical point stress, electric conductivity, etc.

B) LINER INSTALLATION PROCEDURES

Upon arrival on site, perform a "job walk" with the installer's representative to ensure the area to be lined has been prepared for the installation, all dimensions to be confirmed, and the final procedures set out.

If required, all geotextile panels will be placed into position, overlapped and sealed to prevent panel separation. The geotextile will be held in place at the outer or exposed edges using convenient weight material. The prefabricated geomembrane panels will be lifted into position in preparation to unfold. All liner panels must be protected, on site arrival, from damage and must be stored on flat, smooth surfaces prior to placement. Single handling of each panel is recommended to prevent damage. Each panel will be placed into position and weighted on exposed edges. Each panel overlap will be not less than 4" and all overlaps will be checked to ensure they are clean, dry and free of debris.

In all cases, only the number of panels that can be seamed and edge secured during an operational period will be placed. This will prevent damage due to wind lift etc. on unsecured edges. After panel placement, major overlap seams will be welded, then the outer edges anchored or secured. Once the complete membrane is in place, all secondary seaming for piping, booting etc. will be carried out. Using this approach, proper panel placement with expansion wrinkles evenly displaced over the liner can be assured.

All seams will be minimum 1½" in width and where necessary to ensure seal, a cap strip will be welded over the original seam. All seaming will be carried out on hard flat surfaces to ensure quality results. After seaming is complete, all seams will be visually checked and spot tested for quality assurance. These spot checks are recommended at every 50' interval and will be minimum of mechanical point stress type, vacuum or forced air. All seam repairs will be carried out as required and after visual inspection, sheet flaws will be repaired.

All seams will be numbered and any repairs will be noted on daily time tickets. Seam welding techniques will be identified for all field seaming.

Anchoring of the liner will be either of two methods, depending on the type of facility berm. For ground constructed berms, the liner will be set into an anchor trench which has been precut into the berm crown on the outer down slope edge. This trench is recommended as being placed a mimimum of 2' back from the crown. The anchor trench is backfilled using compacted soil, having the liner held in place by either a pretreated 4 x 4 placed into the trench bottom or by backfill only. For concrete or other constructed manmade berms, the liner is secured by use of mechanical bolt sealing techniques using suitable strapping, fastening hardware and compatible gasket material.

Placing containment geomembrane liners under tanks requires that proper design and installation procedures are followed to prevent liner damage. After the proper base has been prepared a 2" - 4" cover of sand should be compacted in place. The liner c/w geotextile underlay and overlay (4mm thickness minimum) is placed on the base area or slid in under a presently raised tank. The liner is centered and unfolded to allow for a minimum of 6" free edge around the outer tank circumference. At this point another cap of sand (4") is placed on top of the liner and levelled. The tank can now be placed into position without damage to the liner.

C) CONTAINMENT OPTIONS

Optional designs or accessories are available for surface containment systems. Some of these options are listed below:

1) Protective berm "skirt"
2) Backfill options using geotextile
3) Draw-off sump design
4) Partial lining
5) Leak detection system installation

A protective "skirt" of similar or different liner material can be included into the containment system for service life extension of the containment liner. In some cases, the necessary containment liner material may be susceptible to U.V. degredation. By covering the main lined area with geotextile/backfill the liner can be protected and a skirt of highly U.V. resistant material placed over exposed berm surfaces and anchored in place.

The main liner can be covered using native soil backfill or prepared gravel. Depending on the liner material, geotextile protective overlay may be placed to prevent surface puncture damage to the liner. If backfill is to be placed, all placement should be carried out in such a manner so that all work is carried out from on top of the placed fill.

Draw off sumps can consist of a membrane lined pit only or auxillary equipment installed to provide fluid draw-off capability from the crown of the berm. This design would prevent the necessity of equipment and/or men working on the liner for pumping out fluids.

Partial linings can be prepared for facilities that now exist; This can include lining under existing tanks that are being repaired/raised. If at some future date the complete facility requires a lining, no further costs are incurred for raising the tank the second time. The remainder of the area can be lined and sealed to the existing under tank liner.

Many leak detection systems are available and can be installed on site either before or after a liner is placed. This is an option well worth consideration.

IV. SECONDARY CONTAINMENT - SUBSURFACE FACILITIES

A) DESIGN CONSIDERATIONS

In order to optimize the installation of a secondary containment geomembrane liner system, a complete set of design and layout drawings is required. Using these drawings, prefabrication for most of the liner system in the fab shop where controlled conditions exist, optimize seaming quality. Difficult field seams can be predone, thus decreasing installation time and cost as well as providing a more assured installation. The ideal geomembrane liner is one that is one piece with no seams. Since this is not possible, the best alternative is a liner that has been shop fabricated under ideal conditions, thereby minimizing field welding.

Design all geomembrane liners to specifications outlined as per governmental regulations and recommended procedures as set out by the membrane manufacturers. Maintain minimum design criteria as listed below:

1) All seams will be minimum 1½" in width.
2) Where possible, all critical seams will be cap welded with a cap strip of identical material.
3) All liners will be designed with an oversize tolerance to prevent stress induced liner failure from irregularities in the excavated areas. This tolerance will be minimum 2% to maximum 10%.
4) All liners will be designed to extend to surface, along with an extra skirt that can be folded over at surface to provide drainage of water away from the interior of the lined facility.

5) Geotextile will be supplied with every installation to provide extra external protection against liner puncture.
6) All geotextile will be nondegradable, antifungal nonwoven material of minimum thickness of 4mm.
7) Where possible, liner seams will not be at fold locations, further assuring against potential stress failures.

Obtain warranty for any geomembrane liner against failure if it meets the material manufacturer's containment criteria. Do not accept warranty for any installation that utilizes a geomembrane liner that is not compatible with the contained fluids. Installations will ultimately be the end user's sole responsibility.

B) SITE PREPARATION

The following will detail the requirements that should be followed in preparation of a site for a geomembrane liner. Once the basic excavation has been completed, the exposed ground should have all large rocks, earth clumps, roots etc. removed and if necessary a layer of sand or equivalent (±4") placed and compacted. This will provide a solid smooth contour for the liner. Regulations will require a floor slope of 20mm/meter to provide for a predesigned sump facility in the excavation. The sides can either be excavated vertically or on 3:1 slopes depending on soil conditions and local safety regulations. Regulations will state that the lined facility must be designed in such a way so that all surface water run off will not enter the lined area. Consequently, if the intended lined area has sloped sides, the final impervious facility cover (i.e. asphalt, concrete) must extend past the edges of the sloped excavation. If this cannot be achieved, design options are available that will meet these requirements. This will be explained in the following sections.

For radiating piping trenches to the pumps, these should be excavated in a manner that will provide a gentle slope back to the main containment area to allow for drainage to the sump. Secondary sumps can be constructed into the trench layouts to provide extra draw off capability as well as monitoring capability to isolate possible future leaks.

C) LINER INSTALLATION

Upon site arrival inspect the prepared facility to ensure it is fully prepared for acceptance of the liner system and that final construction is per original designs for a prefabricated system. The geotextile underlay will be placed into the excavated area as well as any trenches that require it. The geotextile will be placed in such a way that it will totally protect all lined areas up to the crown of the slope. For installations with vertical sides, the geotex will be placed covering the complete sump and fastened to the ground to prevent fall back.

The liner or liner panels are lifted into preset placing on the excavation floor and unfolded into place. The liner (panels) will be placed in order to provide continuous "wrinkle" effect to allow for settlement or liner movement. For excavations with vertical sides, the liner will be prefitted with lifting ropes so that once it is in place on the floor area, the sides can be raised and secured at ground level. The geotextile overlay can now be layed out for internal liner protection and secured.

The liner is backfilled according to tank manufacturer's specifications with care being taken not to damage the liner integrity on the first fill layer. Prior to backfilling the "sump" area, appropriate pump out equipment should be placed and temporarily secured into position.

At this time, the trenching liners can be laid into position and seam welded where necessary. All seaming will be carried out on a hard flat surface and the liner placed after seam quality has been assured. The trench liners can be prefabricated in a manner that sufficient extra material is available so that when the piping and backfill is in place the extra provides a wrap over cover that will prevent water from entering the trenches. The wrap over cover is recommended rather than a sealed cover to allow for future piping access. If the liner has been sealed into a sleeve form, the liner would be damaged by cutting to access the pipes.

The final seam of the trench liner to the sump liner can be completed prior to final piping and backfill placement. After the liner has been fully installed, it is recommended that a nondegradable plastic warning tape be buried several inches above any lined area so that possible future excavation can be prewarned of the lined system.

After all backfill is in place, the extra liner "skirt" can be placed to prevent water entry into the lined area. The "skirt" will either be folded inward at an upslope or left folded outward on a downslope. If required a water shed covering can now be placed into position so that its edges exceed the lined perimeter of the facility. This "water shed" cover can be of a resistant material for burial but does not need to be resistant to the containment fluids, consequently cheaper in price than a complete asphalt cover.

D) CONTAINMENT OPTIONS

Several options are available for use with the geomembrane liner system. These are listed below:

1) Leak detection system under the liner.
2) Water shed cover for lined area.
3) Liner for piping for double wall tank applications.
4) Warning tape for lined facility - on outside of main liner and extending to surface.
5) Geotextile covers for all trenching liners.
6) Individual tank liners instead of complete liner system.

V. SUMMARY

The geomembrane liner system can be adapted to most applications involving protection from leaking or spilled fluids. Most connections required to provide a completely sealed system can be accomplished using material designs and if not, mechanical seal techniques using specialty fittings are available. This system can provide quick, economical and assured secondary containment now, or as a lead in for future requirements.

TABLE A

SECONDARY CONTAINMENT
GEOMEMBRANE MATERIAL TEST REFERENCES

PHYSICAL PROPERTY	PLASTIC FILM LINERS (PE, PVC ETC.)	COATED FABRIC LINERS
Density	ASTM D1505, D792	ASTM D751
Weight	ASTM D1505, D792	ASTM D751
Gauge	ASTM D1593	ASTM D751
Tongue Tear		ASTM D751
Grab Tensile	ASTM D638, D882	ASTM D751, FED.STD. 191-5100
Strip Tensile	ASTM D638, D882	ASTM D751, FED.STD. 191-5100
Tear Resistance-Initiation	ASTM D1004	FED.STD. 191-5134.1
Puncture Resistance	FTMS 101C	FTMS 101B
Hydrostatic Resistance	ASTM D751A	ASTM D751, FED.STD. 191-5512-1
Dimensional Stability	ASTM D1204	ASTM D1204
Elongation	ASTM D471, D638	ASTM D751, ASTM D471
Abrasion Resistance		FED.STD. 191a
Cold Crack	ASTM D746, D1790	ASTM D2136, D2137
Hardness	ASTM D2240, D785, D1415	ASTM D2240, D785, D1415
Coating Adhesion	N/A	ASTM D751, FED.STD. 191-5970
Seam Adhesion	ASTM D638	ASTM D751, D3083, MIL-T-43211
Volatile Loss	ASTM D1203	ASTM D471
Water Absorption	ASTM D570	ASTM D471
Solubility	ASTM D471	ASTM D471
Volume Swell	ASTM D543	ASTM D543
Permeability	ASTM E996	ASTM D814, E996
Rate of Transport	ASTM E996	ASTM D814, D2684
Moisture Vapor Transmission	ASTM E996	ASTM D814
Ozone Resistance	ASTM D1149	ASTM D1149
Soil Burial Resistance	ASTM D3083	
Environmental Stress Crack	ASTM D1693	
Blocking		FED.STD. 191-5872
Trapezoid Tear		ASTM D2263
Chemical Resistance	ASTM D543, D13, D396 D883, D471	ASTM D543, D396, D883, D13, D471

TABLE B

SECONDARY CONTAINMENT

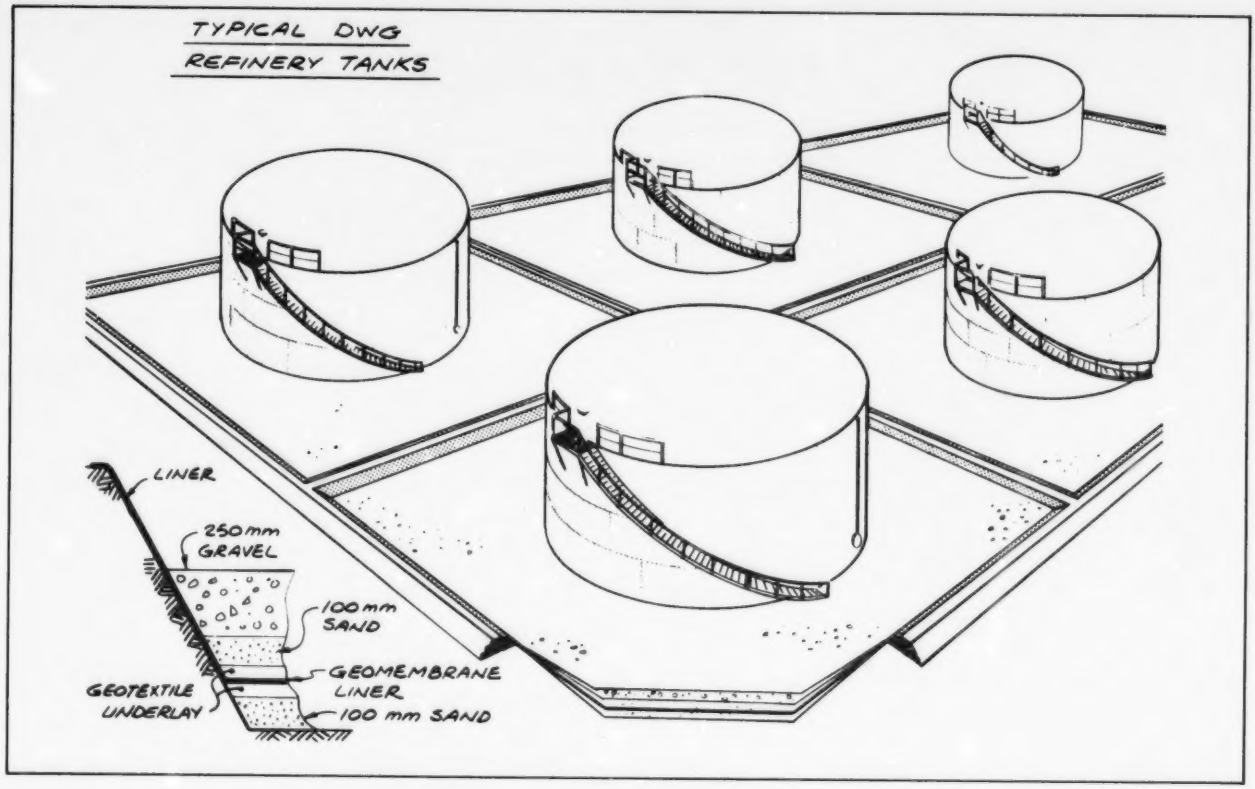
PERMIATION RATE
CONVERSION TABLE

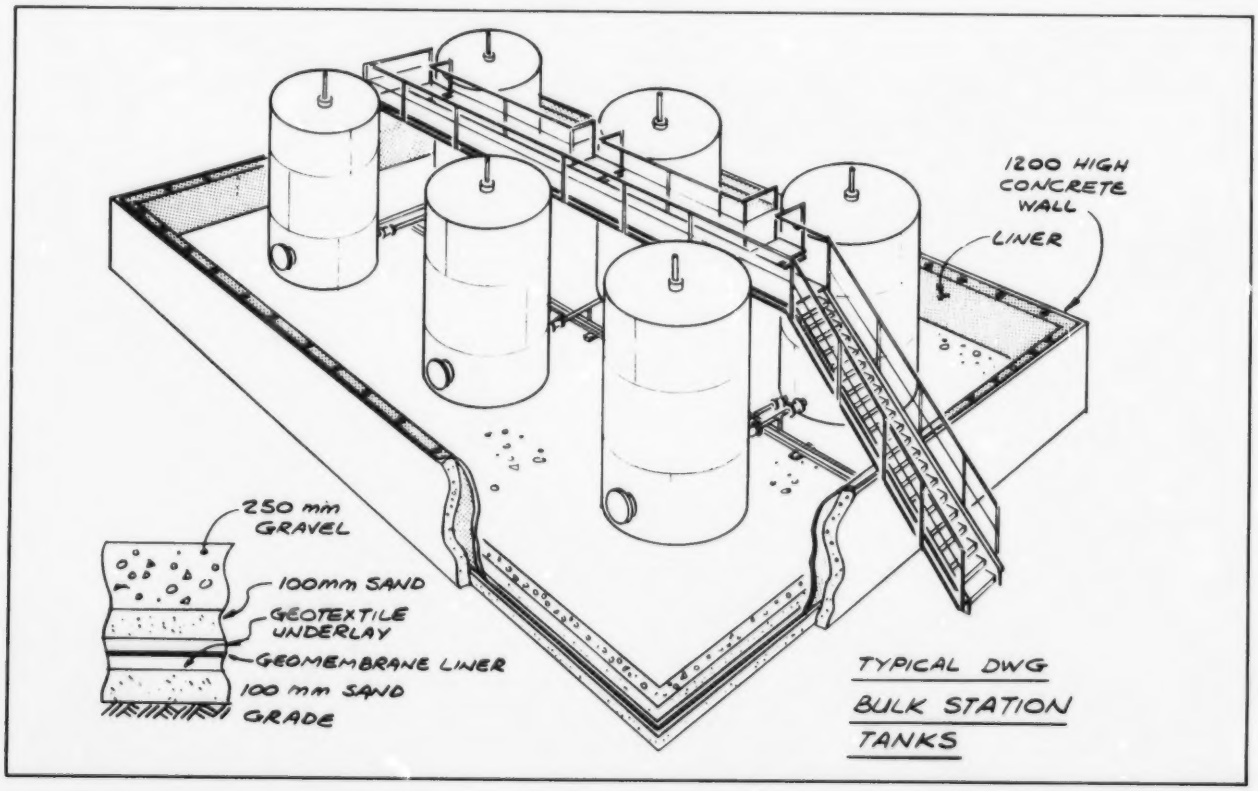
OZ./FT²/DAY	CM/SEC	IMP.GAL/FT²/DAY	LITRES/FT²/DAY	LITRES/M²/DAY
0.01	5×10^{-9}	6.23×10^{-5}	2.84×10^{-4}	3.06×10^{-3}
0.02	1×10^{-8}	1.25×10^{-4}	5.68×10^{-4}	6.12×10^{-3}
0.03	1.5×10^{-8}	1.87×10^{-4}	8.52×10^{-4}	9.17×10^{-3}
0.04	2.0×10^{-8}	2.49×10^{-4}	1.14×10^{-3}	1.22×10^{-2}
0.05	2.5×10^{-8}	3.12×10^{-4}	1.42×10^{-3}	1.53×10^{-2}
0.10	5×10^{-8}	6.23×10^{-4}	2.84×10^{-3}	3.06×10^{-2}
0.20	1×10^{-7}	1.25×10^{-3}	5.68×10^{-3}	6.12×10^{-2}
0.30	1.5×10^{-7}	1.87×10^{-3}	8.52×10^{-3}	9.17×10^{-2}
0.40	2.0×10^{-7}	2.49×10^{-3}	1.14×10^{-2}	0.1223
0.50	2.5×10^{-7}	3.12×10^{-3}	1.42×10^{-2}	0.1529
0.75	3.75×10^{-7}	4.67×10^{-3}	2.13×10^{-2}	0.2294
1.00	5×10^{-7}	6.23×10^{-3}	2.84×10^{-2}	0.3058

EG: If a mat'l is 30 mil it is 0.0762 cm. thick

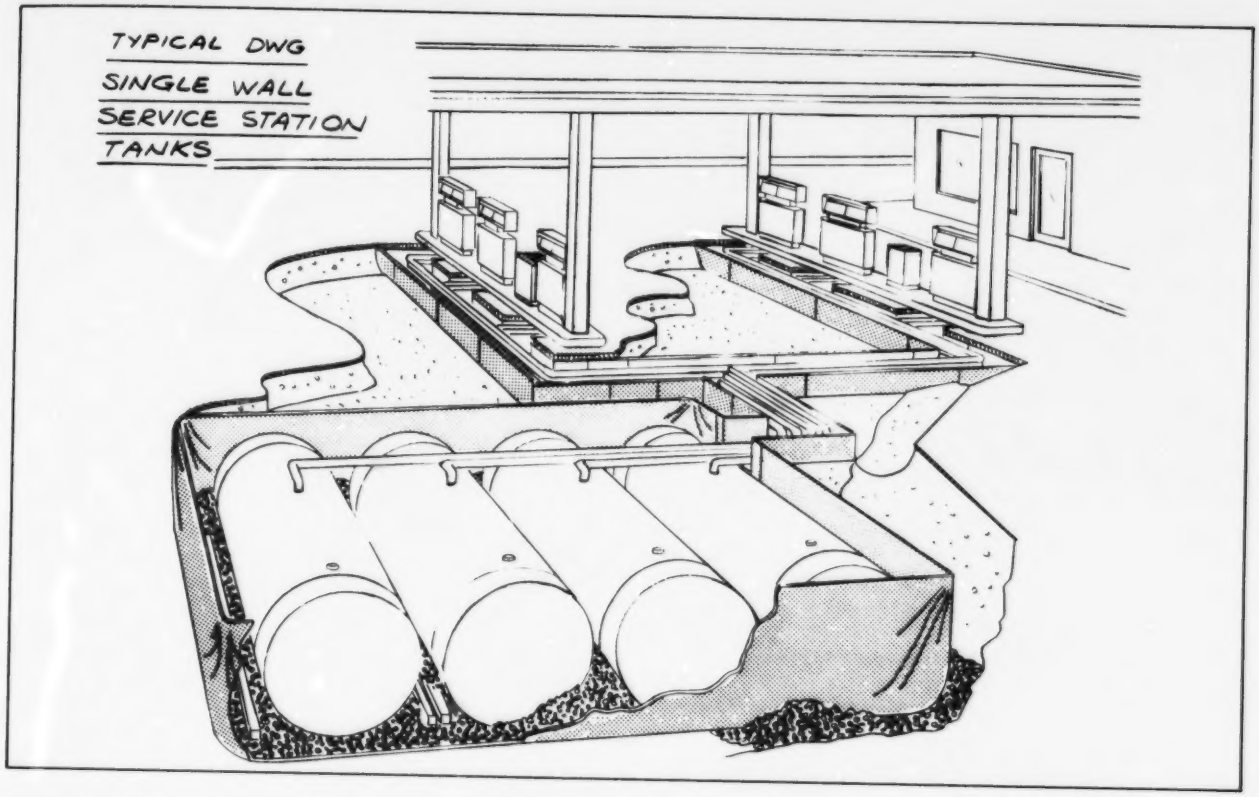
Time to penetration is: $\frac{.0762}{.0000001}$ = 762,000 sec.

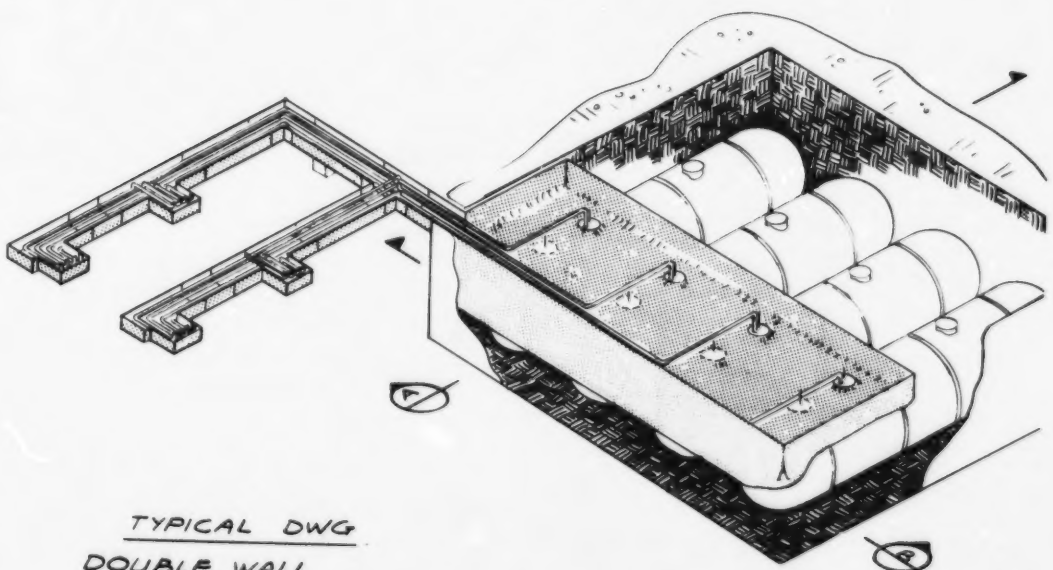
No. days = $\frac{762{,}000}{86{,}400}$ = 8.82 days


TYPICAL DWG
REFINERY TANKS
LINER
250mm GRAVEL
100mm SAND
GEOMEMBRANE LINER
GEOTEXTILE UNDERLAY
100 mm SAND

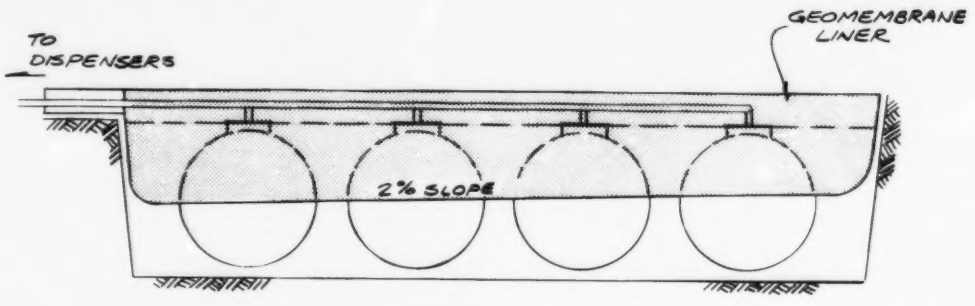

1200 HIGH CONCRETE WALL
LINER
250 mm GRAVEL
100mm SAND
GEOTEXTILE UNDERLAY
GEOMEMBRANE LINER
100 mm SAND
GRADE
TYPICAL DWG
BULK STATION
TANKS

TYPICAL DWG
SINGLE WALL
SERVICE STATION
TANKS





TYPICAL DWG
DOUBLE WALL
SERVICE STATION TANKS



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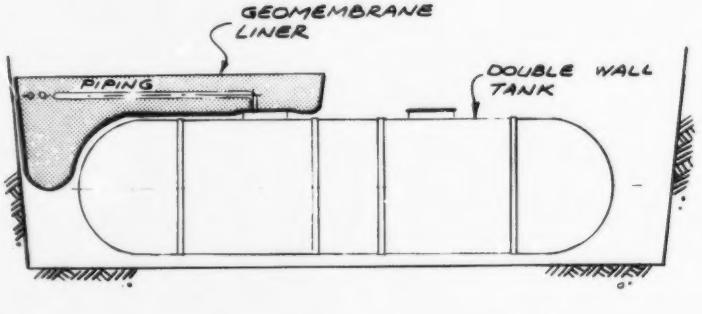
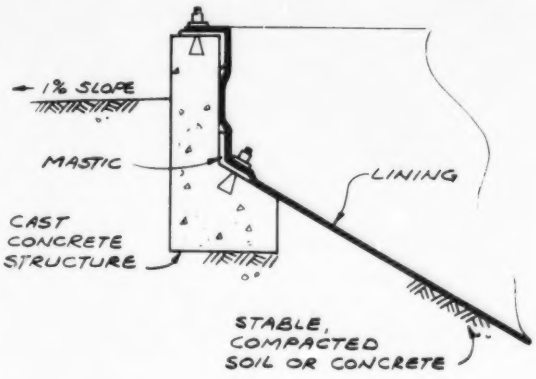
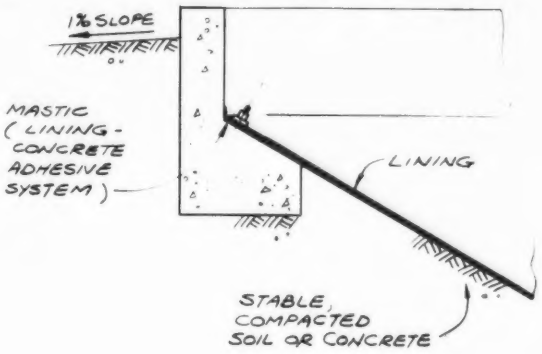
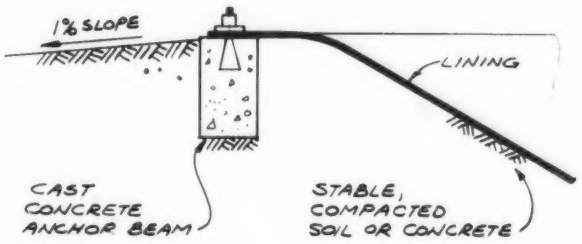
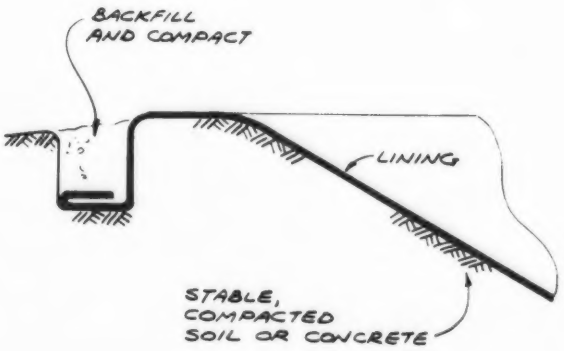


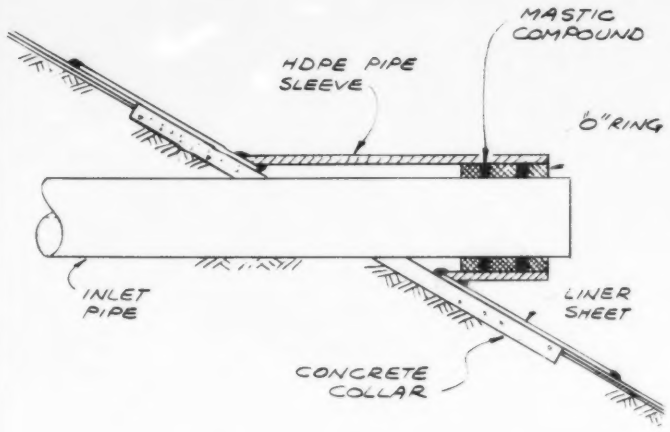
SECTION (A)


1% SLOPE
MASTIC
LINING
CAST CONCRETE STRUCTURE
STABLE, COMPACTED SOIL OR CONCRETE


1% SLOPE
MASTIC (LINING - CONCRETE ADHESIVE SYSTEM)
LINING
STABLE, COMPACTED SOIL OR CONCRETE


1% SLOPE
LINING
CAST CONCRETE ANCHOR BEAM
STABLE, COMPACTED SOIL OR CONCRETE

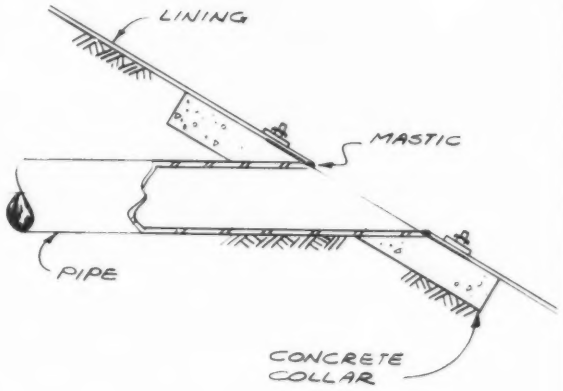

BACKFILL AND COMPACT
LINING
STABLE, COMPACTED SOIL OR CONCRETE

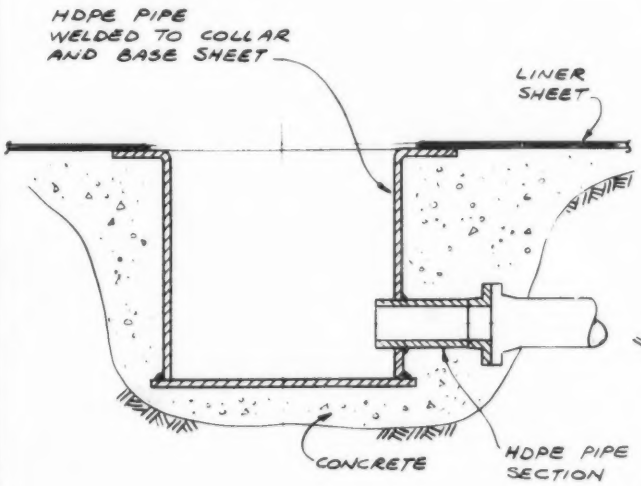


PREFABRICATED SLEEVES ARE INDIVIDUALLY MANUFACTURED FOR EACH PIPE PROTRUSION AND SEALED WITH COMPRESSION "O" RINGS

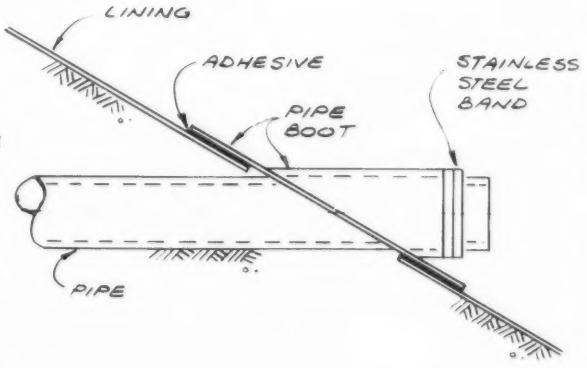
CONNECTION OF LINER SHEET TO CONCRETE OR STEEL INLET PIPE

It is always preferential that penetrations through a liner should be avoided. However if the system dictates penetrations to be a necessity, competent mechanical fastening is possible.





GUARDIAN CAN PROVIDE HDPE SUMPS, PREFABRICATED TO DETAILED SPECIFICATIONS, FOR APPLICATIONS WHERE CONCRETE SUMPS WOULD BE SUBJECT TO CHEMICAL ATTACK.



CONNECTION OF LINER SHEET TO PREFABRICATED HDPE SUMP

NOTE: NOT SUITABLE FOR ASPHALT PANEL LININGS

CROSSLINKED POLYMER ABSORBENT FOR LIQUID CHEMICAL SPILL CONTAINMENT, REMOVAL AND STORAGE

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EcoPlastics Ltd.

O. Meresz,
Ontario Ministry of Environment

INTRODUCTION

Bulk spills of industrial chemicals into water can be major contributors to contamination of water and sediment. The 1985 perchloroethylene spill into the St. Clair River focussed public attention on the lack of effective and safe methods for spill clean-up. The bulk of the perchloroethylene spill was cleaned up by vacuuming pools of the chemical from the river bottom. This necessitated sending divers down to the spill site on a regular basis. At the time of this publication, divers are still visiting the site to remove accumulated perchloroethylene now perculating from the saturated sediment.

EcoPlastics Ltd., with the support of the Ontario Ministry of Environment, targetted the development of a crosslinked polymer absorbent as an alternative river bottom clean-up method. This clean-up method has several advantages:

1. The volume of waste generated in the spill clean-up would be greatly reduced, since the organic chemical is selectively retrieved;
2. The crosslinked absorbent could be placed on the river bottom and retrieved without the need to send down divers;
3. Disturbance of the river bottom would be minimal;
4. Coverage of the spill with the absorbent should minimize dissolution of the chemical into the water body itself.

Uncrosslinked and fibrous synthetic polymers, as well as crosslinked polymers, have been used for the clean-up of chemical spills, as they have a high absorption capacity for organic chemicals and a low affinity for water (Ross et al., 1988). A problem with absorbents made from both polyethylene and polypropylene fibres is that the absorbed chemical is partially released back into the environment when it is retrieved from the spill site (EcoPlastics Ltd., 1989). Currently, no crosslinked polymer absorbents specifically designed for chemical spills are commercially available. Until late 1988, a crosslinked alkylstyrene polymer absorbent (Haigh, 1970) was marketed by Emco Inc. However, it was not cost competitive and was therefore withdrawn from the marketplace.

In this paper, the use of a modified commercially available polymer as an absorbent for specific chemical spills is described. The target spill chemical chosen as an example was perchloroethylene, representing in behaviour a range of chlorinated solvents. The performance of the modified polymer in

both lab and field-simulation trials, as well as its method of production, are presented.

POLYMER CHOICE

The goal of this study was to develop an absorbent for chlorinated hydrocarbons. For this reason, ethylene vinyl acetate (EVA) was chosen as the commercial resin. Upon exposure to a chlorinated solvent, unmodified EVA will absorb the solvent and swell. This characteristic is largely attributed to the vinyl acetate component of the copolymer. Absorption of the solvent continues until the EVA loses its original structural integrity and dissolves in the solvent. In order to allow EVA to be used in solvent retrieval systems, the individual polymer chains must be crosslinked to prevent dissolution and impart structural strength.

As the degree of crosslinking is increased, the strength of the EVA also increases. However, the swelling capacity and therefore the ability to efficiently absorb chemicals decreases. The degree of crosslinking required by a commercial product will, therefore, be a compromise between the requirements of structural strength and maximum absorption or swelling capacity.

CROSSLINKED EVA SHEET

The first method used to produce crosslinked EVA was that of a heated press. Ethylene vinyl acetate (Elvax 150, Dupont) was mixed with varying quantities of the initiator dicumyl peroxide on a two roll mill preheated to 75°C (see Table 1). The mixture was then crosslinked in a Carver press at 165°C and 3000 psig for 2.5 hours, producing a film of approximately 25 mil thickness.

The absorption capacity (g solvent/g polymer) of each sample of crosslinked polymer was measured as follows: A preweighed amount of polymer was placed in tetrachloroethylene and allowed to swell at room temperature for a period of time. In order to separate the swollen polymer from the excess liquid, the mixture was poured over a 14 mesh screen. The swollen polymer, retained on the screen, was shaken and the bottom of the screen was blotted with lint-free tissues until the tissues showed no further wetting. The polymer pieces were then placed in a covered weighing bottle, weighed and returned to the solvent. This process was repeated at appropriate intervals to record the rate of solvent uptake.

To measure the structural integrity of the crosslinked polymers, a more empirical test was used. If the polymer did not dissolve in the solvent, could be picked up and handled with tweezers without disintegrating and did not turn sticky or jelly-like, it was deemed to be structurally strong.

Table 1 shows the effect of added initiator on the capacity of EVA for absorbing solvent. If less than 0.3% (w/w) initiator was used, the polymer became very jelly-like, as if dissolving,

and was easily torn apart. It was not possible to measure the absorption capacities of these samples. At the 0.3% initiator level, the absorption capacity was found to be 49 g of tetrachloroethylene per gram of polymer. However, the swollen polymer still lacked mechanical strength and could not be handled easily. At levels equal to or greater than 0.4% initiator, the swollen polymer was not sticky and at levels greater than 0.4%, the swollen polymer could be handled without breaking. The absorption capacity decreased as the percentage of initiator and therefore the degree of crosslinking, increased. The measured absorption capacities ranged from 49 g solvent/g polymer for the 0.3% initiator material, to 6 g solvent/g polymer for the polymer prepared with 6.0% initiator.

An additional parameter that is important in the clean-up of chemical spills is the time needed to achieve maximum absorption capacity (see Table 1). For the thin films (0.025 in.), this time varied between one and four hours.

The optimum initiator concentration was found to be 0.5% dicumyl peroxide. Crosslinked polymer prepared using this level of initiator picked up 30 times its weight in tetrachloroethylene after 4 hours, while maintaining good structural strength.

Table 1. MAXIMUM ABSORPTION CAPACITY & TIME TO REACH MAXIMUM ABSORPTION CAPACITY VS PERCENT INITIATOR USED IN CROSSLINKING EVA. Crosslinking was carried out by pressing at 165°C for 2 h with dicumyl peroxide as initiator. Sample thickness was 0.025 inches.

INITIATOR (%)	ABSORPTION CAPACITY (g tetrachlorethylene/ g polymer)	TIME TO REACH ABSORPTION CAPACITY (h)	DESCRIPTION
0	-	-	Dissolved
0.3	49	24	Broke on lifting
0.4	35	4	Stable
0.5	30	4	Stable &
1	17	4	stiff
2	10.6	2	enough
4	6.8	1	for
6	6	1	lifting

This method of preparing the crosslinked EVA produced a polymer suitable for spill clean-up, but it is time consuming on a small scale. It would be expensive to produce large quantities of the polymer by this method, unless commercial scale compression molding equipment is used. In an effort to cut down the production time, crosslinked EVA was prepared with varying initiator concentrations in 0.25 in. thick cylinders. The absorption capacities for each sample were determined as described above and are tabulated in Table 2.

The maximum absorption capacity of the crosslinked EVA was found to be independent of the thickness of the polymer at a constant level of initiator. However, the time required to reach that maximum absorption capacity is much greater for the thicker samples than for the thin film samples (Table 1). This difference, 96 hours for a sample 0.25 in. thick versus 4 hours for the sample 0.025 in. thick, may limit application of this product form.

Table 2. MAXIMUM ABSORPTION CAPACITY & TIME TO REACH MAXIMUM ABSORPTION CAPACITY VS PERCENT INITIATOR USED IN CROSSLINKING EVA. Crosslinking was carried out by pressing at 165°C for 2 h with dicumyl peroxide as initiator. Sample thickness was 0.25 inches.

INITIATOR (%)	ABSORPTION CAPACITY (g tetrachloroethylene/ g polymer)	TIME TO REACH ABSORPTION CAPACITY (h)	DESCRIPTION
0	-	-	Dissolved
0.1	-	-	Jelly & sticky
0.2	-	-	Jelly & sticky
0.5	25	96	Stable & stiff
1	16	96	enough for
2	10	96	lifting

CROSSLINKING OF EVA BEADS

In order to overcome some of the limitations described above, a third method of polymer absorbent production, namely crosslinking EVA beads without melting, was therefore developed. Several laboratory scale experiments were conducted to optimize

the procedure, which involved using a solvent to convey the initiator into the EVA pellets and disperse it uniformly, followed by effecting crosslinking during a controlled heat cycle.

Scale-up of the crosslinking procedure to the pilot scale (15 kg) necessitated a number of process changes. A slightly different grade of ethylene vinyl acetate, with a lower melt index, was chosen to prevent meltdown of the beads in the pilot reactor. The initiator was changed from dicumyl peroxide to a lower temperature initiator, lauroyl peroxide. To obtain crosslinked polymer with structural strength similar to the samples made in the heated press, a 0.1% lauroyl peroxide concentration was found to be sufficient.

For the pilot scale production runs, ethylene vinyl acetate (Elvax 265, Dupont, 15 kg) was added to an EcoPlastics custom built reactor, a stainless steel vessel containing a rotating ribbon. The reactor was flushed with nitrogen for one hour, while heating to 40°C. Hexane, containing the desired amount of the dissolved initiator lauroyl peroxide, was added and the beads were soaked for one hour. The reactor was flushed again with nitrogen for an hour, and then heated to 60°C. The beads were heated at this temperature until the initiator had undergone several half-lives, approximately 27 hours.

The curing time was found to be important for optimzing both maximum absorption capacity and structural strength. Figure 1 shows typical curves of absorption capacity (g tetrachloroethylene/g polymer) as a function of time swelling in tetrachloroethylene for crosslinked beads prepared with 0.1% initiator. The beads which were heated for only 16 hours (close to one half-life), had a slightly higher absorption capacity, 18 g solvent/g polymer, than those heated for two half-lives, 14 g solvent/g polymer. However, the beads cured for one half-life began to lose their structural integrity after soaking in tetrachloroethylene for two weeks.

The lower absorption capacities observed in the beads as compared to the crosslinked EVA films, may be due to the higher molecular weight, as well as the lower vinyl acetate content of the EVA base resin.

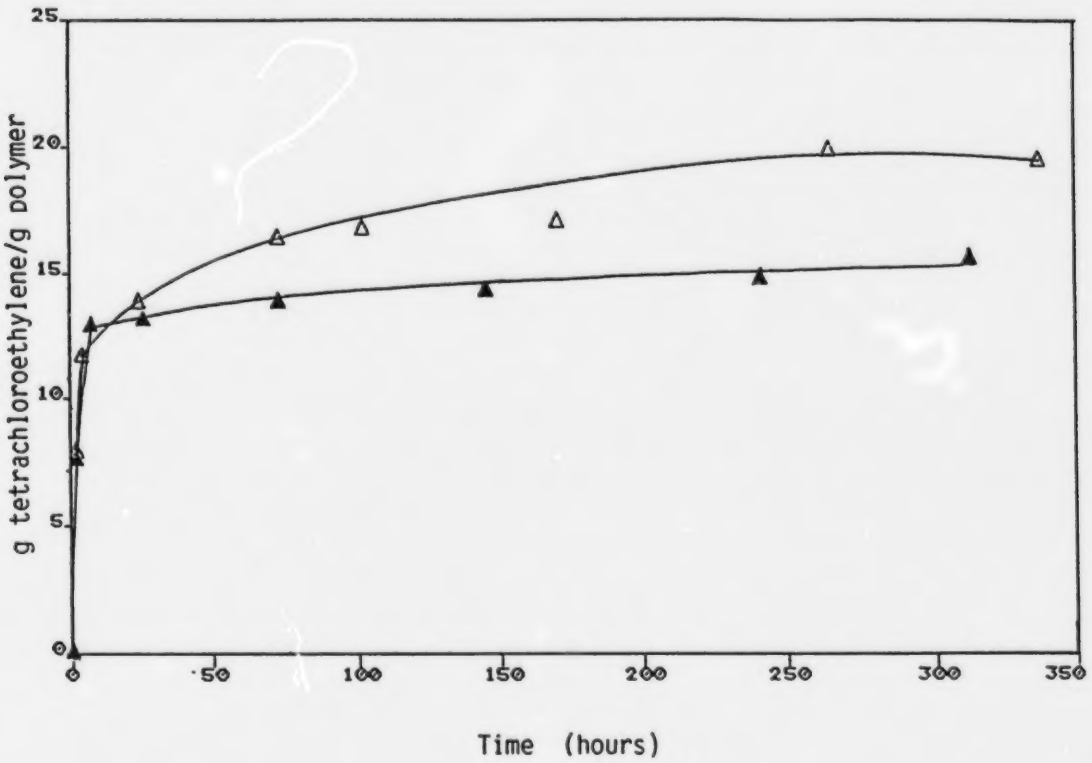

Figure 1. CROSSLINKED EVA BEADS, ABSORPTION CAPACITY VS TIME SWELLING IN TETRACHLOROETHYLENE. Polymer was crosslinked using the low temperature method. The same concentration of initiator (0.1%) was used, but duration of exposure to heat was varied.

16 h heating (△); 27 h heating (▲)

There are several other parameters that are of importance with respect to chemical spill clean-up. These include the desorption from the swollen polymer, recycling of the polymer, and range of chemicals that can be absorbed efficiently.

Desorption from swollen polymer to water

The immobilization and clean-up of the bulk spill is a priority in order to minimize dissolution of the contaminant into the water. The release rate of tetrachloroethylene into water from the swollen polymer was compared to the dissolution of a pool of tetrachloroethylene into water. Crosslinked polymer, fully swollen in tetrachloroethylene, was placed in distilled water and shaken. As a control, the same amount of solvent was placed in distilled water and shaken. After a period of time, the water samples were analysed by gas chromatography for dissolved tetrachloroethylene in water. It was found that although some solvent desorbed into the water from the swollen crosslinked polymer, the dissolution rate was 40% to 60% less than that from the pool of solvent. It was also found that only 0.4% of the solvent absorbed by the beads over a four hour period was desorbed.

Recycling of the polymer absorbent

The crosslinked EVA beads have been reused in 9 cycles of swelling in tetrachloroethylene and drying, without loss of absorption capacity or structural integrity. For application in the clean-up of bulk spills of tetrachloroethylene or other volatile solvents, a system for collecting and recycling the solvent could be devised. Once the chemical has been removed from the absorbent, it can be reused.

Demonstration of range of chemical absorption

The crosslinked EVA was examined for absorption of commonly spilled chlorinated and other organic chemicals. Table 3 shows that the chlorinated solvents were picked up in larger quantities than other organic chemicals. This is to be expected, since EVA has a high affinity for chlorinated hydrocarbons. As illustrated in Table 3, other chemicals are also absorbed to varying degrees.

Table 3. ABSORPTION CAPACITY OF CROSSLINKED EVA BEADS. The polymer was crosslinked using the low temperature method with 0.5% initiator (lauroyl peroxide).

Chemical	Absorption Capacity (g chemical/g polymer)	
	2 h	92 h
Trichloroethylene	16.0	39.7
Tetrachloroethylene	8.9	17.1
Trichloroethane	6.0	11.4
Dichloromethane	6.5	8.0
Trichlorobenzene	3.8	13.1
Toluene	5.1	7.5
Xylene	4.8	7.5
Benzene	4.7	6.3
Gasoline	2.5	3.5
Hexane	0.7	2.5
Methyl Ethyl Ketone	0.5	0.6

Demonstration of pick-up in a river bed simulation

Prior to an actual field trial, scheduled for the summer of 1989, a river bed simulation was set up in a large tank. The crosslinked beads were contained in mats made from netting material and placed upstream from a sand bag blockade in the simulated river bed. A pump was utilized to give a flow rate of 30 cm/s. When tetrachloroethylene was added to the surface of the sediment, the water carried the blobs downstream to where the mats were located. Once in contact with the polymer absorbent, the solvent was absorbed by the beads. After 96 hours, the mats were removed from the river bottom, leaving no residual solvent on the sand. The beads in the mats had absorbed the solvent "spill", and no detectable solvent was released back into the water upon removal of the mats containing the swollen beads from the tank.

Other applications of crosslinked absorbents for hazardous liquids

Other applications for these polymers exist in solidifying hazardous liquid chemical waste, thus reducing the risk of chemical spills during transportation. Solidification of halogenated organic wastes into thermosets is a known method for landfill storage (Suprenant et al., 1988), but the solidified waste should be further encased in a tough shell to prevent leaching of the absorbed chemicals. The crosslinked polymer

described here shows potential for converting hazardous liquids to a solid form. Once solidified, the waste can be transported with a much greater degree of safety and a decreased risk of dispersal into the environment.

The crosslinked polymer could be used in either bead form or in large blocks, depending on the time available for absorption. After transportation to the desired site, the solvent could be recovered from the polymer and collected for reuse or disposal by incineration.

SUMMARY

The use of crosslinked EVA to absorb tetrachloroethylene spills from river bottoms has been described as an example of a crosslinked polymer designed for clean-up of a specific chemical spill. The absorbent material was prepared in either sheet or bead form. The EVA beads were found to have absorption capacities in the 20 g solvent/g polymer range, had good structural integrity after absorption of the spilled chemical, showed a low rate of release into the water stream and were easily placed and retrieved from simulated river beds without detectable loss of the absorbed solvents. The crosslinked polymer could also be used for solidification of hazardous chemicals to make their transportation and storage safer.

ACKNOWLEDGEMENTS

EcoPlastics Ltd. would like to acknowledge financial support from the Ontario Ministry of the Environment.

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PRELIMINARY RESULTS OF REVERSE OSMOSIS AND ULTRAVIOLET PHOTOLYSIS/OZONATION TESTING AT THE PAS SITE - OSWEGO N.Y.

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T. Kady, Environmental Response Team, U.S. EPA
R. Evangelista, R.F. Weston
C. Goulet, Seprotech Systems Inc.

INTRODUCTION

The PAS Superfund site is a former solvent incineration facility in Oswego N.Y. In 1979, drums were removed, lagoons drained and a slurry wall, a cap and a leachate collection system installed. Approximately 780,000 US gallons (2,952,300 litres) of leachate from the site, containing low ppm levels of metals and organics, are collected annually for treatment/disposal. During a trial carried out in August/September 1988, reverse osmosis (RO) and ultraviolet photolysis/ozonation/hydrogen peroxide (UV) were investigated as possible measures for reducing the volume of leachate requiring off-site treatment/disposal.

Reverse Osmosis is a pressure driven membrane process originally developed for the provision of drinking water from salt and brackish sources. It can also be applied to industrial wastewater, chemical spills, and landfill leachates. The water to be treated is passed, under pressure, across the surface of a semi-permeable membrane. A portion of the water and some contaminants then pass through the membrane by a process of solution/diffusion. The remaining stream passes tangentially across the surface of the membrane and is fed back to be mixed with the incoming feed stream. This allows the contaminants in the original feed to be concentrated, while up to 95% of that feed passes through the membrane as cleaner permeate. The removal of contaminants depends upon the materials used in the membrane surface layer. RO membranes will reject inorganic compounds but proper care must be taken to ensure that the organics will neither pass through nor destroy the membrane.

UV photolysis/ozonation/hydrogen peroxide is an enhanced oxidation process. The principal oxidizing agents are radicals having a much greater oxidizing power than their precursors, normally ozone (O3) or hydrogen peroxide (H2O2). The O3, and sometimes H2O2, combine with UV light resulting in a synergistic oxidative effect. If contaminated water in the presence of an oxidant is exposed to short wavelength UV light (<300 nm), particularly light closely matched to the absorption spectrum of the contaminants, a large increase in the rate of contaminant oxidation occurs. Using an enhanced oxidation process, a wide range of organic and inorganic compounds can be quickly oxidized into simpler molecular fragments. This rapid treatment is particularly attractive in environmental remediation technology because it can be used for on-site destruction of the contaminants.

The objective of this trial was to determine the feasibility of using RO and UV photolysis/ozone/hydrogen peroxide oxidation, together or singly, for on-site treatment of leachate and thus greatly reduce the volumes requiring off-site treatment. The purpose of this paper is not to evaluate the feasibility of the technologies. Rather, this paper presents the percent rejections by RO and the percent destruction by UV achieved on the contaminants at the PAS trial. Future papers will detail pretreatment requirements, off-site versus on-site treatment economics, problems encountered, and overall treatment feasibility.

PROCEDURE

Prior to RO or UV treatment, all leachate was pretreated by basification followed by filtration. The first pretreatment step undertaken was the basification of the leachate to pH 10 with 25% NaOH to precipitate the iron. Flocs of metal hydroxide formed in the reaction tank, settled in the lamella clarifier, and were filtered in 5um and 0.2 um cartridge filters (Figure I). Depending on the process being used, the filtered supernatant was then fed either to an inline mixer, where the pH was adjusted to 5 with HCl to remove the $CaCO_3$ as $CaCl_2$, or directly to the UV photolysis equipment. Details of the subsequent procedures in each process are discussed below.

Reverse Osmosis Alone

The pretreated leachate was acidified and pumped to a 550 gallon (2000 litre) feed tank from which the RO unit was fed. A second set of 0.2 um filters was placed in line between the feed tank and the RO unit as a precautionary measure. The leachate was fed at 600 and 800 psi to the membranes and the recycle control adjusted to give a permeate :concentrate flow ratio of 5:1, 8:1 or 10:1 (the concentration ratio). Two 4x40 inch elements from four different manufacturers were used for comparative testing. Samples of RO feed, permeates from individual membrane pairs and concentrate were taken at appropriate intervals for analysis. The concentrate and permeate were then re-injected into the leachate field, as requested by N.Y. Department of Environmental Conservation.

Reverse Osmosis Followed By UV Photolysis/Ozone/Hydrogen Peroxide

In this process scheme, leachate was first treated by RO, then by UV. The leachate was processed by the same procedures as outlined above. The resulting RO concentrate or permeate (as desired for the trial in progress) was fed to the UV unit. The treatment of the RO concentrate or permeate was carried out according to the procedure outlined for UV photolysis/ozonation alone (see below).

Ultraviolet Photolysis/Ozone/Hydrogen Peroxide Alone

The leachate, basified and filtered but not acidified, was fed directly to the UV unit. It was then subjected to O_3 and H_2O_2 treatment alone, or to some combination of O_3, H_2O_2, ultraviolet light, and NaOH. Tests were run in both batch and continuous (flow through) modes. Samples were taken at appropriate time intervals and the effluent was discharged to the leachate field.

UV Photolysis/Ozone/Hydrogen Peroxide Followed By RO

Leachate was first treated in accordance to the procedure for UV/O_3/H_2O_2 alone (see above). In addition, the UV/O_3/H_2O_2 effluent was fed to a 190 gallon (700 litre) tank where the pH was adjusted to 5 with HCl. Next, the UV/O_3/H_2O_2 effluent was processed by the RO unit with the concentrate and permeate recycled to the tank. The recycling allowed for a longer period of testing using the desired system configuration. Samples were taken at appropriate intervals.

The RO unit used in this trial was the Environment Canada mobile unit. It is a diesel powered, trailer mounted, self-contained unit with a nominal capacity of 550 gallons (2000 litres) per hour. The UV unit used was a Solarchem RAYOX unit, transported and operated in a 20 foot box van.

For this trial, all samples were analyzed by gas chromatography for organics and atomic absorption spectroscopy for the metals. For the volatiles organics, analysis involved purge and trap introduction of contaminants to the GC column. The analytical instrumentation was calibrated for the 5-200 ppb range. Above this limit, the accuracy drops off rapidly; therefore, samples were diluted so that the major contaminants would be within the desired concentration range. The wide range of concentrations made this difficult. As a result, some of the higher concentrations reported, particularly for the concentrates, may have an inaccuracy as much as 100 percent. In the case of the metals, the accuracy of the technique used falls off at the lower levels. Those metals reported at very low levels may, therefore, be suspect.

RESULTS AND DISCUSSION

During the leachate pretreatment, it was anticipated that adjusting the pH of the leachate to 10 would precipitate the metals, and that the precipitate could be removed from solution by microfiltration disposable cartridge filters. However, the precipitation process was too slow, and much of the precipitate formed after the filters. To alleviate this problem, a reaction tank and a Lamella clarifier were added to the system which allowed time for the precipitate to form and settle before the cartridge filters. After these additions, there was the need to remove several gallons per hour of sludge from the bottom of the clarifier and to change a set of filters approximately every half hour. This could have been remedied by use of a cross-flow microfiltration system but it was judged not to be cost-effective to bring a unit to the trial site at that stage in the testing. After the field trial had been completed, the efficacity of cross-flow microfiltration was confirmed in laboratory testing using actual leachate from the site. The results are included in Table I.

The calculations for the concentration of the organic compounds are based on the mean for all the tests performed within each process configuration. The mean value for each compound and each membrane are listed in the tables. In addition, the percent rejection by RO was based on the mean feed and permeate concentration for each contaminant. The formula used to calculate % rejections is as follows:

$$\% \text{ Rejection} = \left(1 - \frac{\text{Mean concentration in permeate}}{\text{Mean concentration in feed}}\right) \times 100$$

The rejections achieved for the membranes are categorized as follows:

- excellent - 95% and above,
- good - 85 to 94%
- fair - 70 to 84%
- poor - 69% and below.

RO Alone

Table II lists the mean concentrations of the various organic contaminants in the RO feed and the RO permeates.

Table III shows that there was a wide variation among the membranes in rejection of any given compound, and within an individual membrane type in the rejection of various compounds. With a few exceptions, the rejection of the lower molecular weight chlorinated alkanes and alkenes ranged from poor to fair. The same can be said for acetone. Below benzene in Table III, there is a rapid increase in rejection. These larger molecules are much easier to reject by reverse osmosis membranes. These results, in fact, are similar to those achieved at lower concentrations in earlier studies at the Gloucester Landfill (1, 2).

Membrane I was the superior membrane and would be recommended for any spill clean up of these compounds by Reverse Osmosis. The rejections of organic contaminants was rated good (85%) for 18 out of the 25 compounds evaluated. At first glance, it appears that the Membrane III had the lowest rejection of those tested but this is not consistent with earlier work (1, 2). In fact, it performed almost as well for the first half of the testing as Membrane I. During the trial an accidental system overpressurization occurred which seriously damaged Membrane III and deleteriously affected its performance. The other membranes were not effected by the over pressurization. The percent rejection of organics by Membranes II and IV performance was lower than both Membranes I and III (before overpressurization). Therefore, they are not considered to be appropriate for a clean up involving the organics encountered here.

Heavy metal rejections were higher as a group compared with the organics. Antimony, nickel and arsenic showed good to excellent rejections (Table IV). Membrane I showed the best rejections of heavy metals, while the rejection by Membranes II and IV had greater variability. Once again, the Membrane III results are skewed as a result of the overpressurization damage.

UV Photolysis/Ozonation Alone

Using the same calculation formula and performance categories as for RO rejections, the destructions achieved in the leachate were all either good or excellent except for 1,1-dichloroethene. The weighted mean destruction for all of the organic compounds was 97% (Figure III). The destruction of the aromatics was higher than that for the halogenated or oxygenated alkanes or alkenes of similar molecular weight. Ethylbenzene and the xylenes gave excellent results.

RO followed by UV Photolysis/Ozone/Hydrogen Peroxide Oxidation

Two tests were performed in which the UV unit treated concentrate from the RO. During these tests, the UV unit was run in the batch mode. For the organic contaminants evaluated, the 343 ppm mean total organics made these feeds the most concentrated solutions fed to the UV/O3/H2O2 unit. At those high levels, there was in excess of 95% destruction of 14 out of 22 compounds during the same two hour period used for most UV batch runs (Table VI and Figure II) . It is possible that additional processing may have resulted in higher destructions. This can be seen in Figure III which also demonstrates that the UV/O3/H2O2 reaction rate with the organics is second order in concentration. The performance of the UV/O3/H2O2 unit did not decline due to the concentrated metals present.

Several tests were performed in which the UV system, operated in a batch mode, t ated RO permeate. This combination showed high contaminant removals. Except for acetone, all compounds were removed to at least the 98.7% level (Table VII). The pH of the solution during UV/O3/H2O2 treatment did not appear to have any impact on the efficiency of the process when using permeate as the feed.

RO permeate was also treated by UV in a continuous (flow through) mode. The results of this technique appear, at first glance, to indicate that this sequence of operations was not very efficient (Table VIII). Total removals range from poor to excellent, depending on the contaminant. This drop in performance, compared to the batch operation of the UV/O3/H2O2 unit appears to have been caused at least in part by the overpressurization of the RO membranes which effectively destroyed Membrane III. From that time onward, the combined permeate (from the four membranes) was increasingly rich in organics and inorganics. The mean results for the first two runs using this combination, which took place before the deterioration of the permeate, were excellent and are virtually identical to those in the batch mode (Table IX).

Only one run was attempted using UV treatment of the leachate followed by RO treatment of the UV effluent. Excellent total removals were obtained for 13 of 24 compounds but the results were not as good as had been desired (Table X). This probably could have been improved with slower flow through rates but this combination does not appear to be as effective as the reverse order.

PH Adjustment with Microfiltration

The objective of pH adjustment was to remove the iron so that it would not interfere with the operation of the RO or UV units. The precipitate formed at the various pH's was as follows:

a. pH 9 - 1.276 g/l
b. pH10 - 3.241 g/l
c. pH11 - 4.963 g/l
d. pH12 - 4.455 g/l

Table I data shows that pH 10 was the optimum pH for iron removal. However, the above results with those in Table I reveals that pH 11 produced the greatest amount of precipitate. This may be due to the fact that the precipitate was not all metal hydroxides. The leachate is, however, known to contain at least 800 ppm of calcium. This is probably in the form of CaO and CaCO3. The variance of CaCO3 solubility with NaOH concentration is not known but the solubility of Ca(OH)2 in aqueous NaOH drops rapidly with increasing NaOH concentration. The dark green/brown precipitate was, therefore, probably a mixture of hydrated metal hydroxides and calcium compounds.

CONCLUSIONS

Reverse Osmosis and UV Photolysis/Ozone/H2O2 Oxidation were tested separately and in combination. Varying levels of success in concentration, rejection and destruction were achieved. The applicability of these technologies to problems such as the PAS site will depend upon the surface discharge and reinjection levels for the contaminants set by the regulatory authorities.

REFERENCES

1. H. Whittaker et al; Reverse Osmosis at the Gloucester Landfill; Proceedings of the Technical Seminar on Chemical Spills; Toronto, Ontario; February 5-7, 1985; pages 190-207.

2. H. Donison et al; Development and Demonstration of a Mobile Reverse Osmosis and Adsorption System for Environmental Cleanups; Proceedings of the 4th Technical Seminar on Chemical Spills; Toronto, Ontario; February 10-12, 1987; pages 201-222.

TABLE I

MICROFILTRATION - CONCENTRATION OF METALS (mg/L)

METAL	LEACHATE	pH 9 FILTRATE	pH 10 FILTRATE	pH 11 FILTRATE	pH 12 FILTRATE
Fe	34.27	0.18	0.07	0.17	0.30
As	<0.02	<0.02	<0.02	<0.02	<0.02
Sb	0.03	0.03	<0.02	<0.02	0.02
Pb	0.11	0.22	0.29	0.29	0.44
Ni	1.30	0.97	1.04	1.04	0.98
Zn	0.11	0.10	0.02	<0.02	0.02

TABLE II

RO RESULTS - MEAN CONCENTRATION OF ORGANICS

COMPOUND (ug/l)	LEACHEATE FEED (ug/L)	PERMEATE (ug/L)			
		I	II	III	IV
DICHLOROMETHANE	26666.7	14828.7	8677.3	11306.9	4749.6
ACETONE	26813.1	5841.8	11567.6	19361.5	15987.6
1,1-DICHLOROETHANE	1103.6	84.0	284.8	494.6	278.3
1,1-DICHLOROETHENE	1099.0	237.7	1289.9	2378.9	277.1
1,2-DICHLOROETHANE	2214.0	348.1	886.4	1109.6	867.9
t-1,2-DICHLOROETHENE	22082.2	7937.1	16339.7	10102.7	14435.5
1,1,1-TRICHLOROETHANE	819.9	36.2	147.8	243.6	120.2
TRICHLOROETHENE	266.2	74.2	112.0	181.2	85.2
BENZENE	921.1	66.8	379.7	397.3	401.1
BROMODICHLOROMETHANE	677.5	60.9	151.8	202.7	129.9
METHYL ISOBUTYL KETONE	151.2	15.2	25.3	33.1	20.8
BROMOFORM	31031.9	111.0	1346.1	3871.5	528.7
TETRACHLOROETHANE/ENE	332.4	78.8	64.5	268.5	176.3
TOLUENE	7934.6	424.2	2550.6	3225.7	1457.5
CHLOROBENZENE	1393.1	116.6	582.2	564.8	369.8
ETHYLBENZENE	5745.4	173.7	1303.2	2001.1	702.5
m,p-XYLENE	8615.1	221.1	1548.2	2985.5	862.5
o-XYLENE	13352.7	299.7	2391.4	5339.5	1702.5
PHENOL	1911.0	122.0	327.0	1038.0	534.0
DICHLOROBENZENE	100.0	3.0	24.0	56.0	13.0
2-METHYLPHENOL	937.0	14.0	143.0	357.0	149.0
4-METHYLPHENOL	3115.0	71.6	292.0	2085.0	717.0
2,4-DIMETHYLPHENOL	992.0	16.0	158.0	661.0	175.0
BENZOIC ACID	10920.0	48.3	690.0	2823.0	399.0
BIS(2-ETHYLHEXYL)PHTHALATE	80.0	8.0	17.0	38.0	8.0

TABLE III

MEAN RO RESULTS - ORGANIC COMPOUNDS
(% rejections)

COMPOUND	MEMBRANE TYPE			
	I	II	III	IV
DICHLOROMETHANE	44.4	67.5	57.6	82.2
ACETONE	78.2	56.9	27.8	40.4
1,1-DICHLOROETHANE	92.4	74.2	55.2	74.8
1,1-DICHLOROETHENE	78.4	(-17.4)	(-116.5)	74.5
1,2-DICHLOROETHANE	84.3	60.0	50.0	60.8
t-1,2-DICHLOROETHENE	63.9	25.7	54.2	34.6
1,1,1-TRICHLOROETHANE	95.6	82.0	70.2	85.3
TRICHLOROETHENE	72.1	57.9	31.9	68.0
BENZENE	92.7	58.9	56.9	56.5
BROMODICHLOROMETHANE	91.0	77.6	70.1	80.8
METHYL ISOBUTYL KETONE	89.9	83.3	78.1	86.2
BROMOFORM	99.6	95.7	87.5	98.3
TETRACHLOROETHANE/ENE	76.2	80.6	19.2	46.7
TOLUENE	94.7	67.9	59.3	81.6
CHLOROBENZENE	91.6	58.2	59.5	73.5
ETHYLBENZENE	97.0	77.3	65.2	87.8
m,p-XYLENE	97.4	82.0	65.3	90.0
o-XYLENE	97.8	82.1	60.0	87.2
PHENOL	93.6	82.9	45.7	72.1
DICHLOROBENZENE	97.0	76.0	44.0	87.0
2-METHYLPHENOL	98.5	84.7	61.9	84.1
4-METHYLPHENOL	97.7	90.6	33.1	77.0
2,4-DIMETHYLPHENOL	98.4	84.1	33.4	82.4
BENZOIC ACID	99.6	93.7	74.2	96.3
BIS(2-ETHYLHEXYL)PHTHALATE	90.0	78.8	52.0	90.0

TABLE IV

RO RESULTS
METALS - CONCENTRATION ug/L/% REJECTED

COMPOUND	FEED	I	II	III	IV
LEAD	23.0	17.7 / 23.0	24.3 / (-5.7)	31.7 / (-37.8)	23.3 / (-1.3)
ANTIMONY	6.0	1.0 / 83.3	1.0 / 83.3	1.7 / 71.7	1.0 / 83.3
ZINC	41.8	13.6 / 67.5	25.8 / 38.3	32.2 / 23.0	32.1 / 23.3
NICKEL	1638.9	171.1 / 89.6	50.0 / 96.9	817.8 / 50.1	142.2 / 91.3
ARSENIC	41.6	1.0 / 97.6	2.2 / 94.7	26.9 / 35.3	7.9 / 81.0

TABLE V

UV PHOTOLYSIS / OZONE/HYDROGEN PEROXIDE OXIDATION OF LEACHATE - MEAN RESULTS

COMPOUND	FEED (PPB)	UV EFFLUENT (PPB)	% DESTROYED
DICHLOROMETHANE	4360.2	418.5	90.4
1,1-DICHLOROETHANE	495.0	60.8	87.7
1,1-DICHLOROETHENE	286.0	53.9	81.2
1,2-DICHLOROETHANE	1138.6	350.8	69.2
t-1,2-DICHLOROETHENE	4920.4	96.9	98.0
1,1,1-TRICHLOROETHANE	304.1	37.1	87.8
TRICHLOROETHENE	113.7	21.6	81.0
BENZENE	547.8	16.9	96.9
BROMODICHLOROMETHANE	155.8	14.1	90.9
METHYL ISOBUTYL KETONE	54.7	4.5	91.8
BROMOFORM	8004.0	56.5	99.3
TETRACHLOROETHANE/ENE	314.0	13.8	95.6
TOLUENE	3496.3	21.2	99.4
CHLOROBENZENE	659.7	10.4	98.4
ETHYLBENZENE	3086.7	1.1	100.0
m,p-XYLENE	4941.2	1.0	100.0
o-XYLENE	6905.4	2.1	100.0

TABLE VI

BATCH UV TREATMENT OF RO CONCENTRATION
MEAN CONCENTRATIONS

COMPOUND	UV EFFLUENT 120 MIN (ug/L)	UV EFFLUENT 180 MIN (ug/L)	% UV REMOVAL
DICHLOROMETHANE	1733.6	7204.2	5.4
ACETONE	48905.1	--	--
1,1-DICHLOROETHANE	813.2	924.6	68.9
1,1-DICHLOROETHENE	387.1	601.5	--
1,2-DICHLOROETHANE	2774.3	2934.7	39.3
t-1,2-DICHLOROETHENE	552.8	758.9	96.9
1,1,1-TRICHLOROETHANE	168.8	1.0	99.9
TRICHLOROETHENE	81.6	1.0	98.6
BENZENE	117.5	92.9	96.3
BROMODICHLOROMETHANE	527.4	766.8	12.4
METHYL ISOBUTYL KETONE	134.8	176.7	--
BROMOFORM	1762.6	2484.1	98.5
TETRACHLOROETHANE/ENE	241.2	460.6	--
TOLUENE	895.9	386.4	97.0
CHLOROBENZENE	59.6	1.0	99.9
ETHYLBENZENE	22.1	6.9	99.9
m,p-XYLENE	2.5	1.0	100.0
o-XYLENE	1.0	1.0	100.0
PHENOL	0.0	28.0	99.6
2-METHYLPHENOL	50.0	1.0	100.0
4-METHYLPHENOL	64.0	11.0	99.9
2,4-DIMETHYLPHENOL	0.0	0.0	100.0
BENZOIC ACID	11513.0	27860.5	--

TABLE VII

BATCH UV TREATMENT OF RO PERMEATE
MEAN CONCENTRATIONS

COMPOUND	RO FEED (ug/L)	UV 120 MIN (ug/L)	% TOTAL REMOVAL
DICHLOROMETHANE	18662.8	142.7	98.7
ACETONE	32901.9	3097.5	76.9
1,1-DICHLOROETHANE	1576.1	2.7	99.7
1,1-DICHLOROETHENE	578.5	35.2	97.4
1,2-DICHLOROETHANE	3163.9	5.5	99.7
t-1,2-DICHLOROETHENE	34699.1	3.7	100.0
1,1,1-TRICHLOROETHANE	1240.0	1.3	99.8
TRICHLOROETHENE	229.2	1.0	99.8
BENZENE	1308.6	0.8	99.9
BROMODICHLOROMETHANE	731.7	1.0	99.9
METHYL ISOBUTYL KETONE	259.9	1.0	99.5
BROMOFORM	26116.9	2.5	99.9
TETRACHLOROETHANE/ENE	429.5	2.8	98.5
TOLUENE	13835.3	2.4	100.0
CHLOROBENZENE	2292.9	1.0	99.8
ETHYLBENZENE	9913.7	0.6	100.0
m,p-XYLENE	14345.8	0.7	100.0
o-XYLENE	24788.5	1.0	100.0
PHENOL	1987.3	0.5	99.9
2-METHYLPHENOL		0.0	100.0
4-METHYLPHENOL	4083.9	0.0	100.0
2,4-DIMETHYLPHENOL	1304.6	0.0	100.0
BENZOIC ACID	794.9	0.0	100.0

TABLE VIII

CONTINUOUS (FLOW THROUGH) UV TREATMENT OF RO PERMEATE

COMPOUND	RO FEED	% RO REMOVAL	% UV REMOVAL	% TOTAL REMOVAL
DICHLOROMETHANE	18662.8	13.5	90.0	91.4
ACETONE	32901.9	78.6	65.0	92.5
1,1-DICHLOROETHANE	1576.1	74.7	77.9	94.4
1,1-DICHLOROETHENE	578.5	76.0	83.3	96.0
1,2-DICHLOROETHANE	3163.9	51.3	55.5	78.3
t-1,2-DICHLOROETHENE	34699.1	--	97.0	90.3
1,1,1-TRICHLOROETHANE	1240.0	79.6	77.8	95.5
TRICHLOROETHENE	229.2	14.6	84.8	87.1
BENZENE	1308.6	11.8	93.4	94.2
BROMODICHLOROMETHANE	731.7	100.0	90.9	100.0
METHYL ISOBUTYL KETONE	259.9	37.2	87.9	92.4
BROMOFORM	26116.9	100.0	99.3	100.0
TETRACHLOROETHANE/ENE	429.5	38.7	90.5	94.2
TOLUENE	13835.3	--	97.8	93.5
CHLOROBENZENE	2292.9	--	94.6	84.7
ETHYLBENZENE	9913.7	100.0	93.9	100.0
m,p-XYLENE	14345.8	--	--	95.0
o-XYLENE	24788.5	75.9	83.7	96.1
PHENOL	1987.3	52.1	98.4	99.2
4-METHYLPHENOL	4083.9	26.9	98.7	99.0
2,4-DIMETHYLPHENOL	1304.6	0.0	99.3	99.3
BENZOIC ACID	794.9	100.0	99.9	100.0

TABLE IX

CONTINUOUS (FLOW THROUGH) UV TREATMENT OF RO PERMEATE FIRST TWO RUNS (ug/L)

COMPOUND	RO FEED(ug/L)	Ro Perm/ UV FEED (ug/L)	UV PRODUCT (ug/L)	% RO REJECTION (ug/L)	% UV DESTRUCTION	% REMOVAL
DICHLOROMETHANE	3188.3	504.8	39.9	84.2	92.1	98.7
ACETONE	41498.9	3455.4	1656.9	91.7	52.0	96.0
1,1-DICHLOROETHANE	2180.5	257.7	5.8	88.2	97.7	99.7
1,1-DICHLOROETHENE	854.5	60.1	4.3	93.0	92.8	99.5
1,2-DICHLOROETHANE	4359.4	704.6	74.5	83.8	89.4	98.3
t-1,2-DICHLOROETHENE	22969.5	5426.6	12.2	76.4	99.8	99.9
1,1,1-TRICHLOROETHANE	1082.7	62.6	7.9	94.2	87.4	99.3
TRICHLOROETHENE	218.9	31.9	0.4	85.4	98.7	99.8
BENZENE	1730.5	1491.4	9.4	13.8	99.4	99.5
BROMODICHLOROMETHANE	699.1	22.0	0.0	96.9	100.0	100.0
METHYL ISOBUTYL KETONE	66.4	8.9	0.0	86.6	100.0	100.0
BROMOFORM	17827.7	19.7	0.0	99.9	100.0	100.0
TETRACHLOROETHANE/ENE	405.8	102.0	0.9	74.9	99.1	99.8
TOLUENE	17731.0	2164.1	12.8	87.8	99.4	99.9
CHLOROBENZENE	2943.1	434.8	0.4	85.2	99.9	100.0
ETHYLBENZENE	12793.7	954.1	0.1	92.5	100.0	100.0
m,p-XYLENE	19546.0	1263.4	0.0	93.5	100.0	100.0
o-XYLENE	34403.1	2211.6	0.0	93.6	100.0	100.0
PHENOL	1310.0	360.5	3.0	72.5	99.2	99.8
4-METHYLPHENOL	3407.0	457.5	0.0	86.6	100.0	100.0
2,4-DIMETHYLPHENOL	1195.0	314.0	0.0	73.7	100.0	100.0
BENZOIC ACID	0.0	0.0	7.5			

TABLE X

CONTINUOUS (FLOW THROUGH) UV FOLLOWED BY RO TREATMENT MEAN CONCENTRATIONS

COMPOUND	UV FEED (ug/L)	UV PROD (ug/L)	RO PERM (ug/L)
DICHLOROMETHANE	16765.6	1670.9	1445.7
ACETONE	27268.1	9531.4	2036.3
1,1-DICHLOROETHANE	806.1	178.2	45.0
1,1-DICHLOROETHENE	746.5	124.9	30.0
1,2-DICHLOROETHANE	2289.8	1018.5	496.5
t-1,2-DICHLOROETHENE	10514.8	318.8	1017.1
1,1,1-TRICHLOROETHANE	552.7	122.9	25.1
TRICHLOROETHENE	401.6	60.9	52.0
BENZENE	914.6	60.0	52.9
BROMODICHLOROMETHANE	623.2	56.5	0.0
1,2-DICHLOROPROPANE	74.3	18.6	0.0
METHYL ISOBUTYL KETONE	113.6	13.7	8.6
BROMOFORM	32016.1	226.1	0.0
TETRACHLOROETHANE/ENE	475.5	45.2	27.7
TOLUENE	3508.3	75.5	277.9
CHLOROBENZENE	768.2	41.1	117.5
ETHYLBENZENE	2832.0	171.8	0.0
m,p-XYLENE	4566.5	--	226.2
o-XYLENE	7479.2	1222.2	294.3
PHENOL	7632.0	121.0	58.0
2-METHYLPHENOL	1619.0	20.0	15.0
4-METHYLPHENOL	5027.0	67.0	49.0
2,4-DIMETHYLPHENOL	812.0	6.0	6.0
BENZOIC ACID	31526.0	46.0	0.0

FIGURE III UV/O3/H2O2 TREATMENT OF PERMEATE

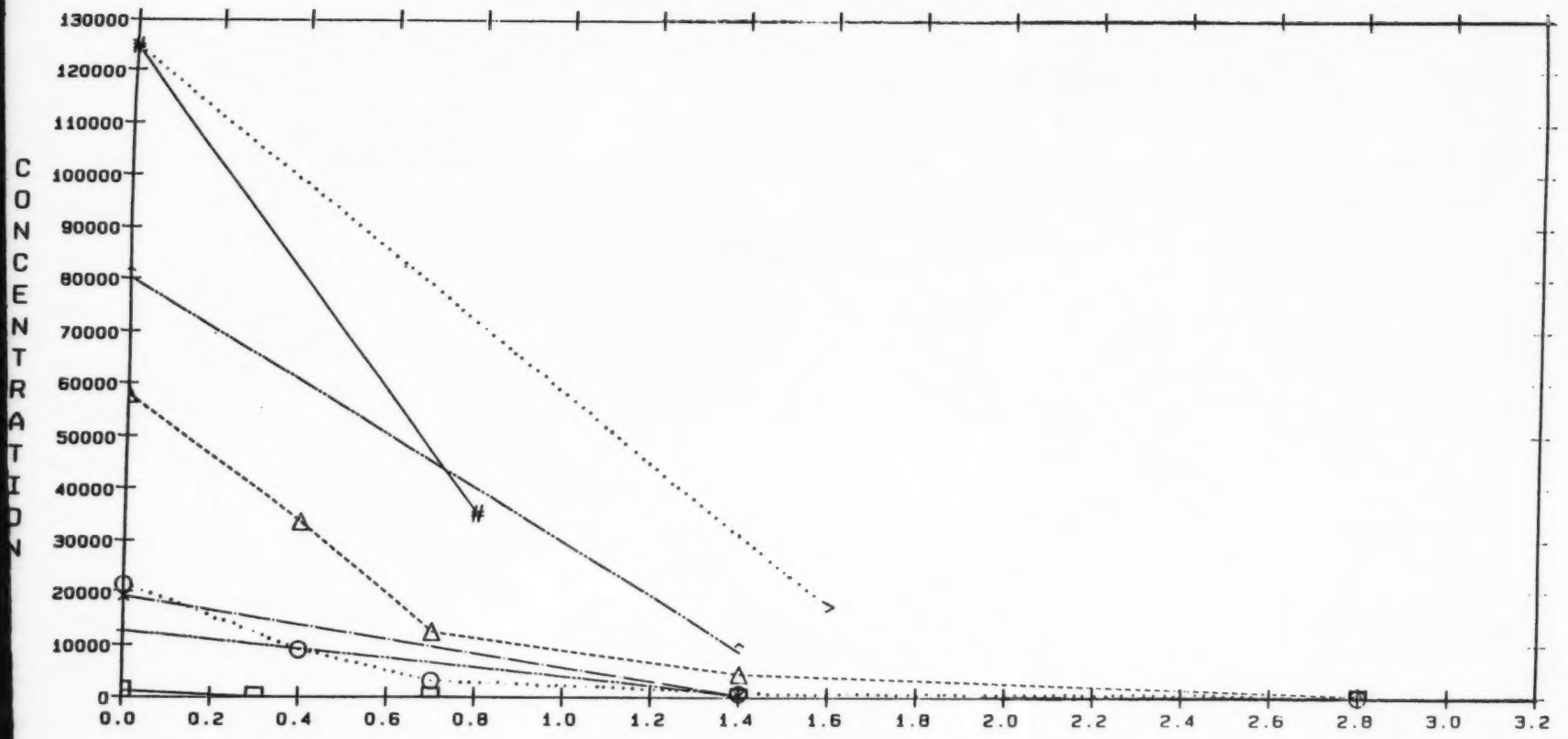


FIGURE II UV/O3,H2O2 TREATMENT OF CONCENTRATE

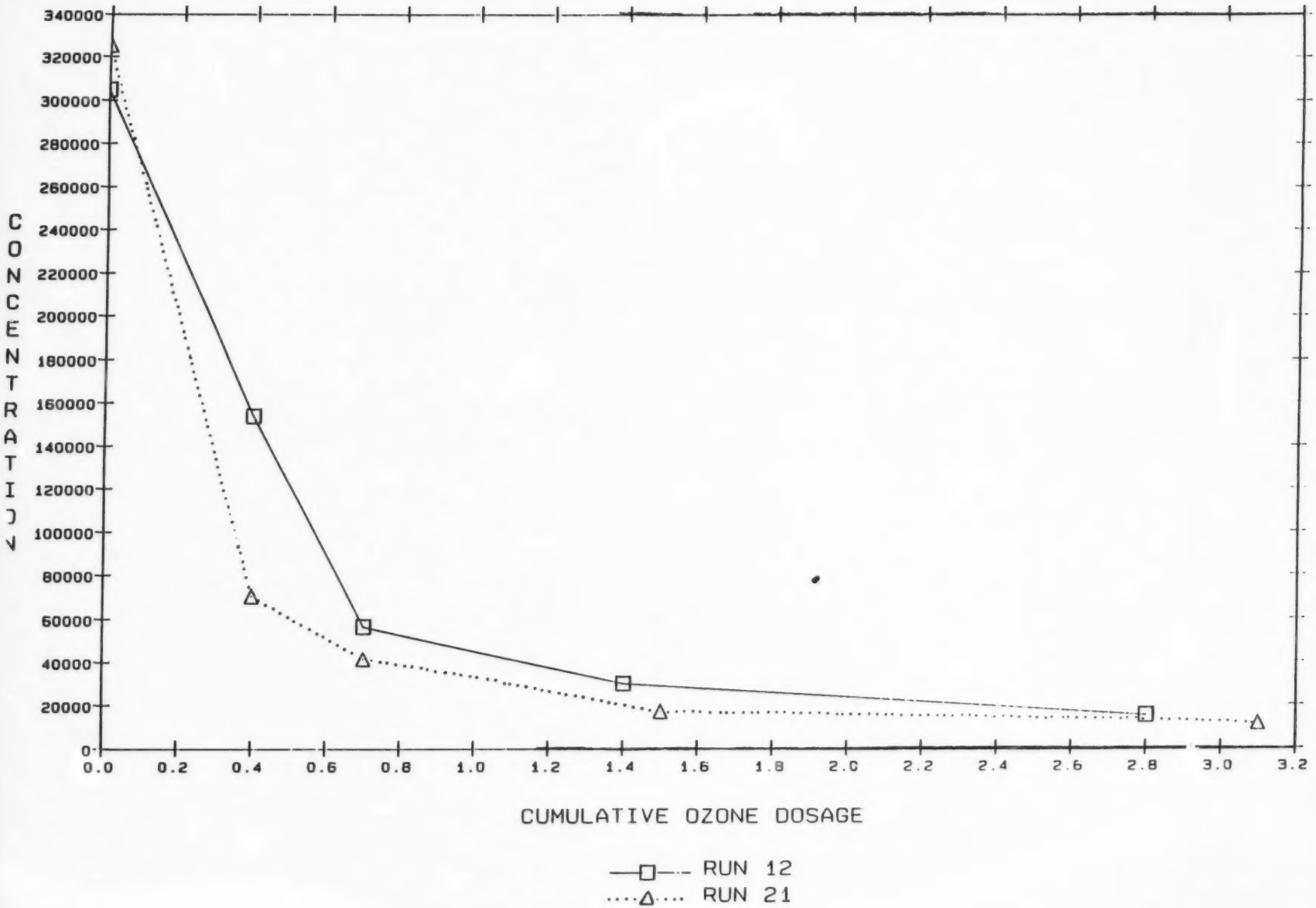
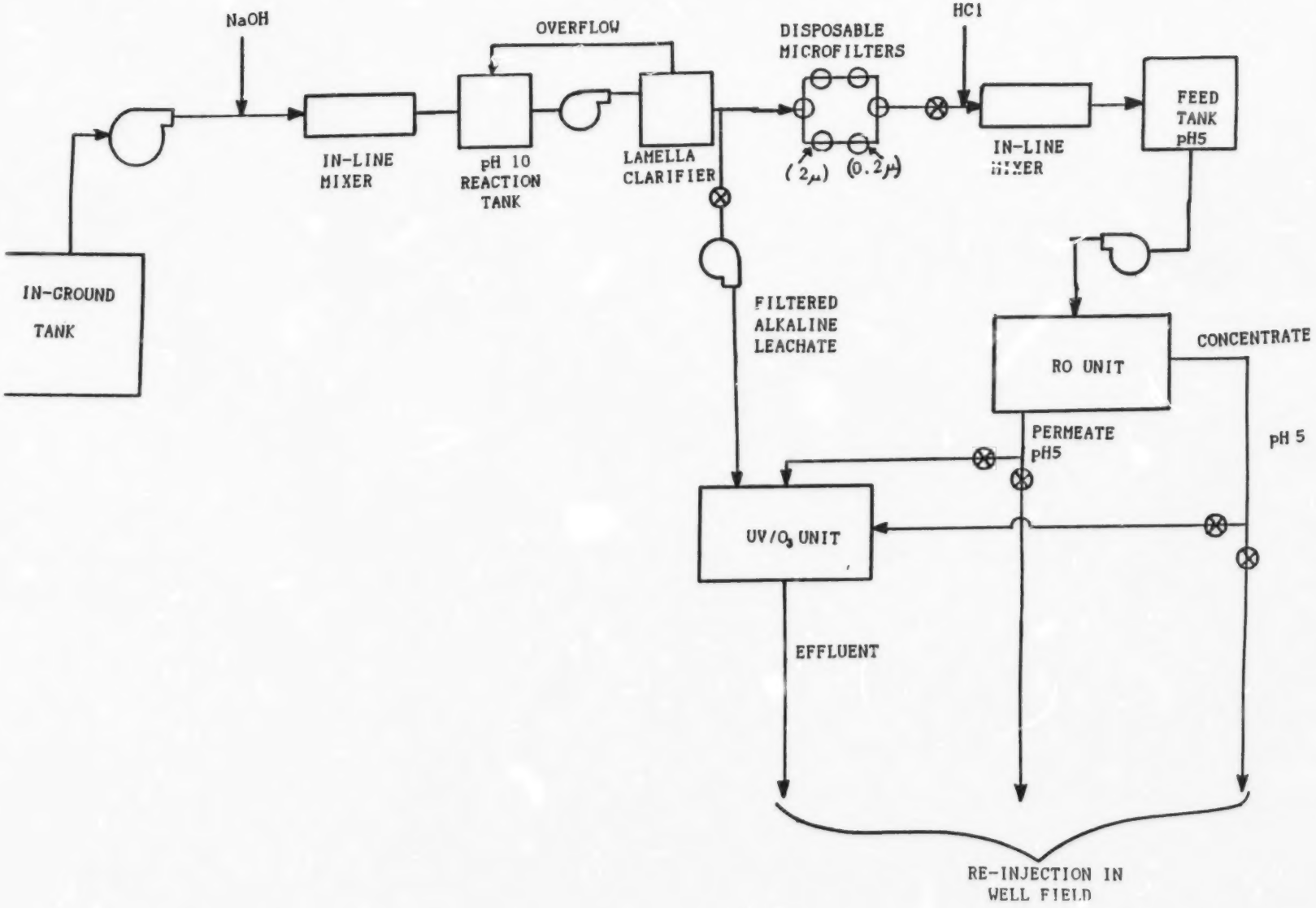


FIGURE 1

LEACHATE TREATMENT SET-UP



Use of Pilot Scale Reciprocating Plate Extraction Column to Remove Organic Contaminants from Water

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INTRODUCTION

Environment Canada is supporting an investigation of the use of liquid extraction (LE) as a method of removing organic contaminants from water. The long term objective is to design a mobile unit which can be transported to the sites of various emergency incidents. Possible incidents include transportation accidents, areas of groundwater contamination due to leaking underground tanks or leaking landfills and chemical spills at industrial sites.

Liquid extraction is used extensively in industry to separate chemical streams. It has been shown to be effective in removing phenols from waste water effluents (1-7) and shows potential for removal of other organics from water (8-10). Although LE is a proven process in industry, little is known about its capabilities and limitations in removing organic contaminants such as alcohols, chlorinated aliphatics, aromatics and ketones from waste waters.

In the first phase of this work a search has been made for suitable solvents by studying the equilibrium partitioning of selected organic solutes between water and selected organic solvents. The four solvents were chosen to represent a variety of functional groups so that general predictive relationships can be developed between a solvent's molecular structure and its effectiveness as an extractant. The ten solutes chosen represent a cross-section of Environment Canada's list of most frequently spilled chemicals. Lab scale experiments have been conducted to measure the partition coefficients (K_{sw}) of the solutes between each solvent and water. Effects of variations in temperature and solute concentration were examined.

The second phase of this work involves the operation of a pilot scale liquid-liquid extraction column. The feed water, contaminated with two test chemicals (toluene and 1,1,2,2-tetrachloroethane), was contacted with an isoparaffinic solvent (Isopar M) manufactured by Esso Chemical Canada Limited. The experiment considered the effects of solvent to water flow ratios and of which phase was dispersed. The mass transfer data accumulated from the lab and pilot scale experiments will be used to design a mobile liquid extraction unit.

BACKGROUND

Liquid extraction is preferred over biological methods of treating waste water when the contaminant has economical value since LE conserves rather the destroys the solute (3,4,10,11). LE is also less susceptible to changes in the feed concentration. This is especially advantageous for a system which will be designed for variable and uncertain feed conditions. Performance of the solvent can be expected to vary slightly with temperature (2,7,12); in general, partition coefficients increase at lower temperatures.

Solvent Selection

The choice of solvents requires a balance between the selectivity and the capacity of the solvent (13-15). The selectivity of a solvent is a measure of how effectively the solute is removed from the water while capacity is a measure of how much solute can be removed by a given volume of solvent. The limit to capacity is defined by the equilibrium partition coefficient of the solute, K_{sw}:

$$K_{sw} = C_s/C_w \qquad [1]$$

For a given concentration of feed, C_w, the concentration of solute in the solvent, C_s, cannot exceed the concentration determined by equation [1]. Usually, solvents with high selectivity have low capacity and therefore large volumes of solvent are required to extract the solute (3,10). Solvents with high capacity tend to be more soluble in water than those with low capacity. Both these factors can contribute to substantial solvent loss.

Other factors which can influence solvent selection are cost, toxicity, availability, flammability, safety and physico-chemical properties such as thermal stability, melting and boiling points, vapour pressure, solubility in water, water uptake, chemical reactivity, and corrosion properties (14,15).

The gap between selectivity and capacity can be bridged by using a mixture of solvents. Mixtures of two solvents, usually one polar solvent and one volatile solvent have been shown to be more effective than either of the two solvents alone (1,3-7,11). However, the use of mixed solvents may make the solvent recovery process more complex. For the single solvent removal of chlorinated hydrocarbons and aromatics from water, kerosene is recommended as a "broad brush" solvent (8,9). This aliphatic solvent is relatively non-toxic, sparingly soluble in water and effectively extracts a large number of contaminants.

Thermodynamic models such as UNIFAC and ASOG can be used to estimate activity coefficients of various solutes in given solvents in an attempt to determine partition coefficients and hence the suitability of the solvents for liquid extraction (14, 16-20). The partition coefficient can be written in terms of fugacity, f. At equilibrium,

$$f_s = f_w \qquad [2]$$

where the subscripts s and w refer to the solvent and water phases respectively. So,

$$x_s\gamma_s = x_w\gamma_w \qquad [3]$$

where x is the mole fraction of the solute, and
γ is its activity coefficient.
Then, if the partition coefficient is defined on a molar basis,

$$k_{sw} = x_s/x_w = \gamma_w/\gamma_s \qquad [4]$$

The thermodynamic partition coefficient, k_{sw}, is related to K_{sw} as defined in [1] since the concentration of the solute, C, is the mole fraction, x, divided by its molar volume, v. Then,

$$K_{sw} = C_s/C_w = (x_s/v_s)/(x_w/v_w) = k_{sw}^*(v_s/v_w) \qquad [5]$$

If the activity coefficient of the solute in the solvent is minimized the partitioning is maximized. Values estimated by the UNIFAC method are being compared to

experimental results for partition coefficients in an attempt to provide a model to guide the choice of solvents for specific spills. At present, these procedures are valuable guides but they are not a substitute for experimental measurement.

LE Equipment

On an industrial scale, it is generally accepted that some form of mechanical agitation is required to ensure sufficient contact for mass transfer of the solute from the water to the solvent (21). This mixing ranges from a stirrer in a batch mixer-settler to rotating or pulsating plates in a countercurrent contacting column. One type of column is the reciprocating plate column (RPC) designed by Karr in 1959. A series of plates is arranged along a vertical shaft, which is reciprocated by an electrical drive to impart a pulsating energy to the liquid in the column. The pulses cause the dispersed phase to break up into small droplets, increasing the area available for mass transfer. The open-type plates have a large free area fraction (0.60) which allows for a high throughput with a reduced tendency to channel. The RPC is versatile and flexible and can handle emulsifiable material (22).

Mass transfer within the column can be optimized by adjusting either the throughput to the column, the intensity of agitation or the plate spacing. At higher throughputs, the efficiency of the column decreases (21). Agitation can be adjusted by changing either the frequency or the amplitude. An increase in agitation causes a finer dispersion of droplets, hence increasing the area available for mass transfer. The plate spacing can be adjusted to maintain an even dispersion throughout the length of the column. As the solute concentration increases in the column, the interfacial tension of the system decreases rapidly as does the energy required for mixing. Since the reciprocating frequency is constant at all points within the column, the plates are placed further apart in the sections of the column in which the solute concentration is high, to reduce the energy imparted to the liquid at that point (21,23). The plate material can also affect mass transfer if the dispersed phase coalesces on the plates (24,25). Each of the above parameters is limited by the flooding point in the column. Flooding is defined as occuring when an emulsion layer forms in the middle of the plate stack and expands to fill the entire plate stack. It can be reversed by reducing the frequency of agitation or the throughput (26).

Once pilot scale tests have been conducted, the scale up of RPC's is straight forward (27). The plate spacing and amplitude are maintained while the frequency, F, is adjusted slightly when scaling from a pilot scale column (1) to a larger diameter column (2):

$$F_2/F_1 = (d_2/d_1)^{-0.14} \qquad [6]$$

The efficiency of the column, defined by HETS (height equivalent to a theoretical stage), will increase with the diameter by a simple power law as well:

$$(HETS)_2/(HETS)_1 = (d_2/d_1)^n \qquad [7]$$

where n has been found to be 0.38 for difficult extractions and decreases for easier extractions. Baffles are introduced to large diameter columns to reduce the effects of axial mixing (27,28).

In order to make LE systems economical, the solute must be recovered from the solvent (29,30). The process used depends on the properties of the compounds involved and can include a second extraction process, distillation or steam stripping.

The literature also contains discussions of several processes related to solvent extraction which may or may not be effective for organics in water. In supercritical

fluid extraction (31-33) the solvent (usually CO_2) is kept at a high pressure so that extraction occurs in the supercritical region. Although the use of non-toxic CO_2 as a solvent is attractive for environmental purposes, the method is only effective for sparingly soluble, volatile organics. A membrane process using solvent extraction principles has also been suggested (34). A third alternative is the use of predispersed solvent to extract solutes from water (35).

EXPERIMENTAL METHODS

Laboratory Scale Partitioning Measurements

The equilibrium partition coefficients for each solute in each solvent and water were measured at three concentrations and three temperatures using a shake flask method. The solutes and solvents considered are listed in Table 1. The solutes were chosen as a representative cross-section of frequently encountered chemicals. The list includes ketones, substituted aromatics, chlorinated and non-chlorinated aliphatics and alcohols. The solvents were chosen to contain and hence characterize various functional groups. Dichloromethane and ethylbenzene are both regarded as "toxic" substances so their suitability for use as extraction solvents will have to be considered carefully before using them in the environment. There is however, a strong physical-chemical justification for investigating their capabilities.

Analysis of all samples has been performed by gas chromatography. The solvent phase and the water phase for highly soluble compounds were analysed by a packed column direct injection GC while the volatile compounds in the water phase were measured on a capillary column purge and trap GC. Mass balances and partition coefficients were determined from these analyses.

Table 1. Solutes and Solvents

SOLUTES	SOLVENTS
acetone	dichloromethane
toluene	ethylbenzene
ethylbenzene	octane
styrene	octanol
1,2-dichlorobenzene	Isopar M
1,2-dichloroethane	
1,1,2,2-tetrachloroethane	
n-hexane	
phenol	
2-ethyl-1-hexanol	

Pilot Scale Studies

Pilot scale experiments were performed on a 5.0 cm inner diameter RPC shown schematically in Figure 1. The column is manufactured of pyrex glass with neoprene gaskets, while the plates and shaft are of stainless steel. Twenty-five plates were used with spacing ranging from 2.5 to 7.5 cm for a total plate height of 125 cm. The amplitude of reciprocation was 2.0 cm and the frequency was 150 rpm. Isopar M was chosen as the solvent for the pilot scale tests. It is a petroleum distillate fraction in the range of C_{11}-C_{16} and was indicated as a potentially good "broad brush" solvent due to its kerosene-like nature. This was confirmed when the equilibrium partition coefficient (K_{sw}) was determined for the test chemicals (Table 2). Since Isopar M is

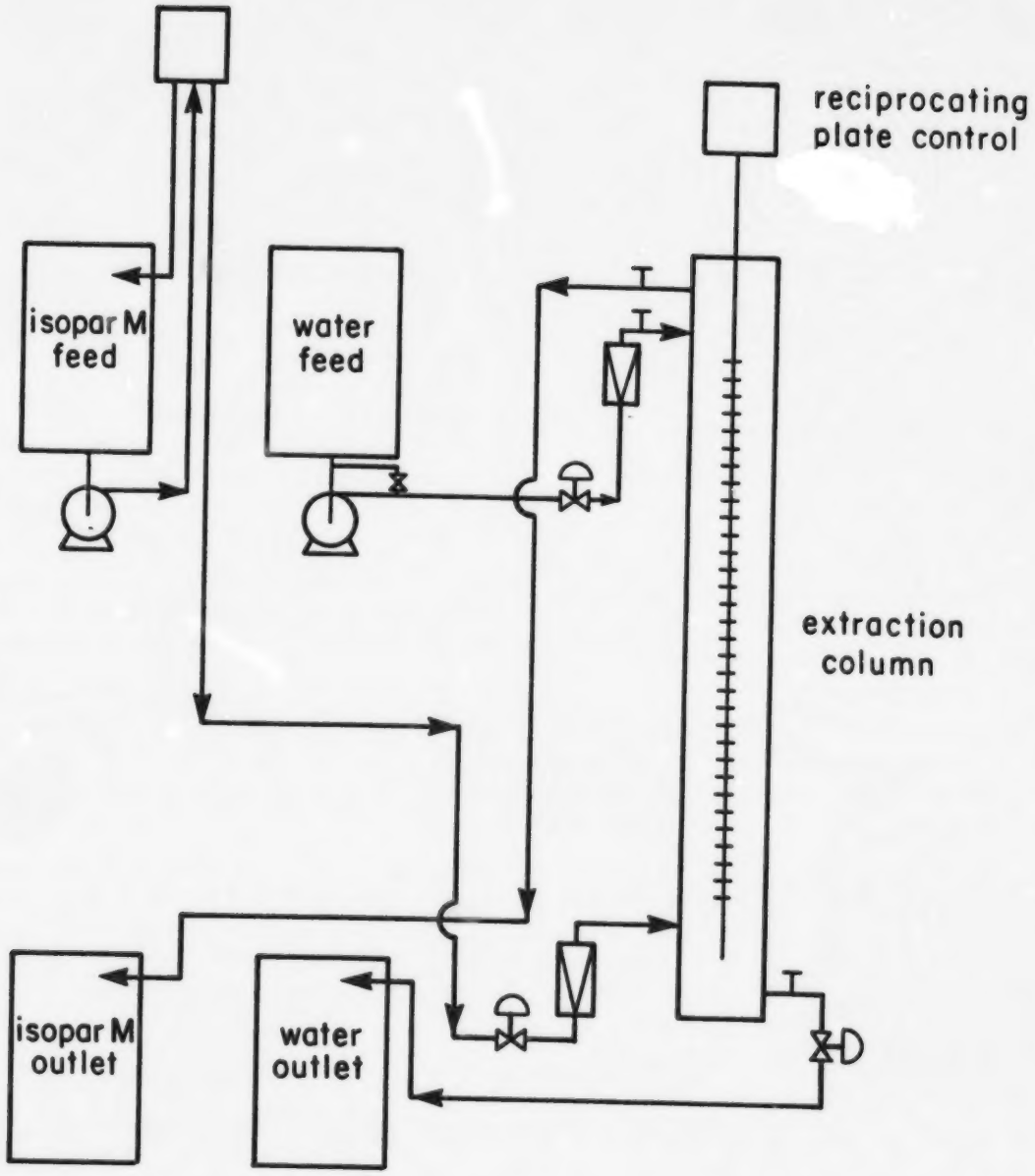

Figure 1. Schematic of pilot scale apparatus

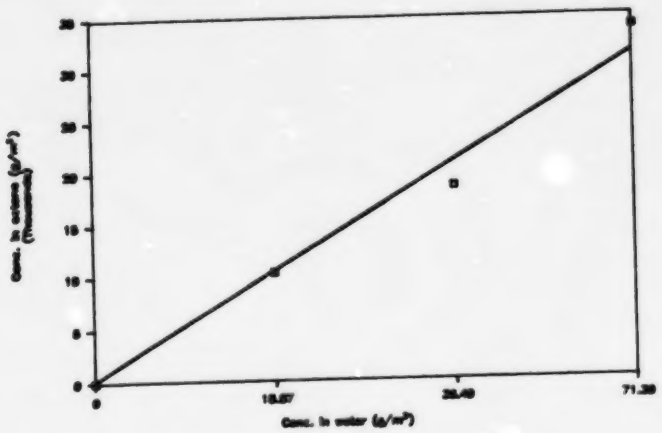

Figure 2. Concentration plot for toluene–octane–water system at 25 °C

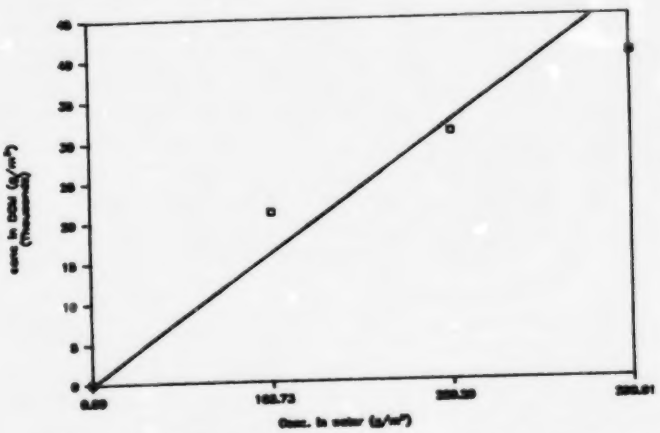

Figure 3. Concentration plot for 1,2–DCE–DCM–water system at 25 °C

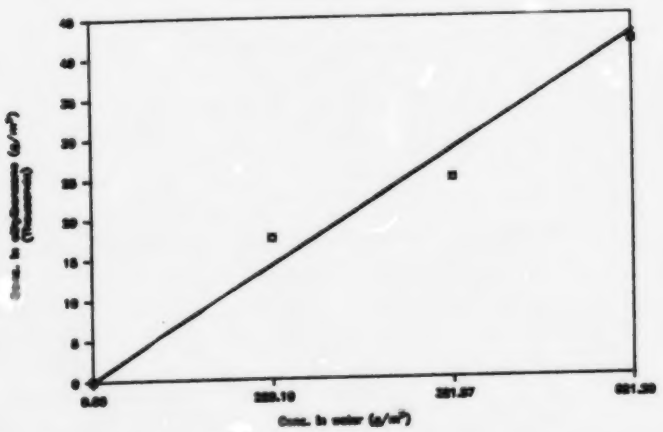

Figure 4. Concentration plot for 1,2–DCE–ethylbenzene–water system at 25 °C

Table 3. Summary of Results for Three Equilibrium Systems

Temp. (°C)	Conc.	1,2-dce-ethbenz-water K_{sw}	% diff. in Mass Balance	1,2-dce-dcm-water K_{sw}	% diff. in Mass Balance	toluene-octane-water K_{sw}	% diff. in Mass Balance
5	low	76.92	3.3	121.3	-4.4	576.4	45.4
	mid	83.34	10.0	130.9	-3.5	549.1	26.1
	high	72.69	-3.5	106.1	-22.3	453.3	10.4
15	low	81.94	-1.0	169.8	9.0	558.1	41.6
	mid	75.60	3.3	154.9	1.4	530.3	25.5
	high	70.11	-11.9	174.3	3.0	469.2	14.3
25	low	76.50	-5.3	204.0	2.1	544.4	18.7
	mid	77.25	0.6	140.5	-0.3	507.6	7.0
	high	67.11	-15.4	138.8	-2.5	473.9	-2.2

at 5 and 15 °C) show very large deviations, which may be due to sample contamination after the 25 °C analysis was completed.

Although the K_{sw} has a ten-fold range for the different solutes, it is clear that the partitioning for hydrophobic solutes is high. (So far, the only solute analysed which does not show a high K_{sw} is acetone, a very hydrophilic compound.) Therefore, LE is potentially a very effective method for removing organic contaminants from water. Theoretically, very low solvent to water ratios can be used (as low as 1/60), depending on the limiting solute to be removed. In practice however, the mass transfer limitations make such low S/W ratios inefficient. Table 4 shows the percent removal obtained from a theoretical single stage extraction process operating at a S/W ratio to 1/20. Even higher efficencies would be obtained in a counter-current contactor.

Pilot Scale Experiments

Six runs were completed on the pilot scale apparatus (Table 5). The solvent to water ratio was changed for each run but the amplitude, frequency of agitation and plate spacing were maintained constant. The first run was performed with Isopar M dispersed in water while the remainder had water dispersed in the continuous solvent phase.

When Isopar M was dispersed in the water phase, solute removal efficiency was unexpectedly low. This is believed to be due in part to the high interfacial tension of the Isopar/water system (24) which reduces the mass transfer of the solute. When the solvent is dispersed, flooding occurs at a lower agitation level, therefore there was not sufficient mixing to compensate for the high interfacial tension of the system. In the cases in which water is dispersed, more vigorous mixing is possible without flooding the column.

Table 4. Removal of Solute in a Single Stage Process (with S/W ratio of 1/20)

K_{sw}	C_w/C_{wo}	Percent Removal
60	1/4	75
100	1/6	83
200	1/11	91
600	1/31	97
3000	1/151	99

Table 5. Summary of Pilot Scale Experiments.

Run	Dispersed Phase	S/W Ratio	Water Flow (mL/min)	Percent Removal	
				Toluene	TECE
1	Isopar M	1/10	830	20-70	15-60
2	water	1/10	830	95-99	86-99
3	water	1/20	1030	99	86-92
4	water	1/30	830	97-99	78-96
5	water	1/20	750	99	85-98
6	water	batch	925	68-92	25-81

The high partition coefficients indicated by the equilibrium experiments imply that very low S/W ratios can be used. In practice, ratios of 1/10 are considered low for a countercurrent system but ratios as low as 1/50 have been used successfully in a RPC (30). Even at S/W flowrate ratios of 1/30, the column is operating with a theoretical excess of solvent. The solvent to water ratio could theoretically be less than 1/100, bringing the operating line nearly parallel to the equilibrium line. However, operation at such low S/W ratios is not pratical since the agitation provided by the column cannot disperse the small amount of solvent evenly through the water to give efficient mass transfer. A compromise between mechanical energy provided to the column and cost of excess solvent must be reached while maintaining sufficient solute removal. One option would be to reflux the solvent. Reflux is not possible for the existing system so it was decided to run the system in a semi-batch operation.

For RUN 6, the column was filled with Isopar M and then solvent flow was stopped. Water was fed into the column at 925 mL/min and samples were taken hourly for 9 hours. Removal was effective at first but dropped quickly for TECE as the capacity of the solvent for TECE was met. The removal of toluene dropped slightly towards the end of the run. It is noted that at no point is the percent removal as high as in the countercurrent flow situation. This can be attributed to the decreased concentration gradient in the semi-batch configuration. It is possible that situations which do not require 99% removal can benefit from a semi-batch operation or the solvent could be cycled continuously. The solvent would have to be replaced before the removal efficiency dropped below the desired level.

Discussion of the LE process is not complete until the problem of treating the contaminated solvent is addressed. For relatively volatile solutes, steam stripping is an attractive solute recovery process. The solvent is heated to approximately 100 ^{o}C to eliminate condensation of the steam which is bubbled through the solvent to remove the solute. If the boiling point of the solute approaches the initial boiling point of the solvent, the effectiveness of steam stripping is greatly reduced. For higher boiling compounds, offsite distillation or incineration of the solvent may be required. The present concept for a mobile extraction column and solute recovery system is illustrated schematically in Figure 5.

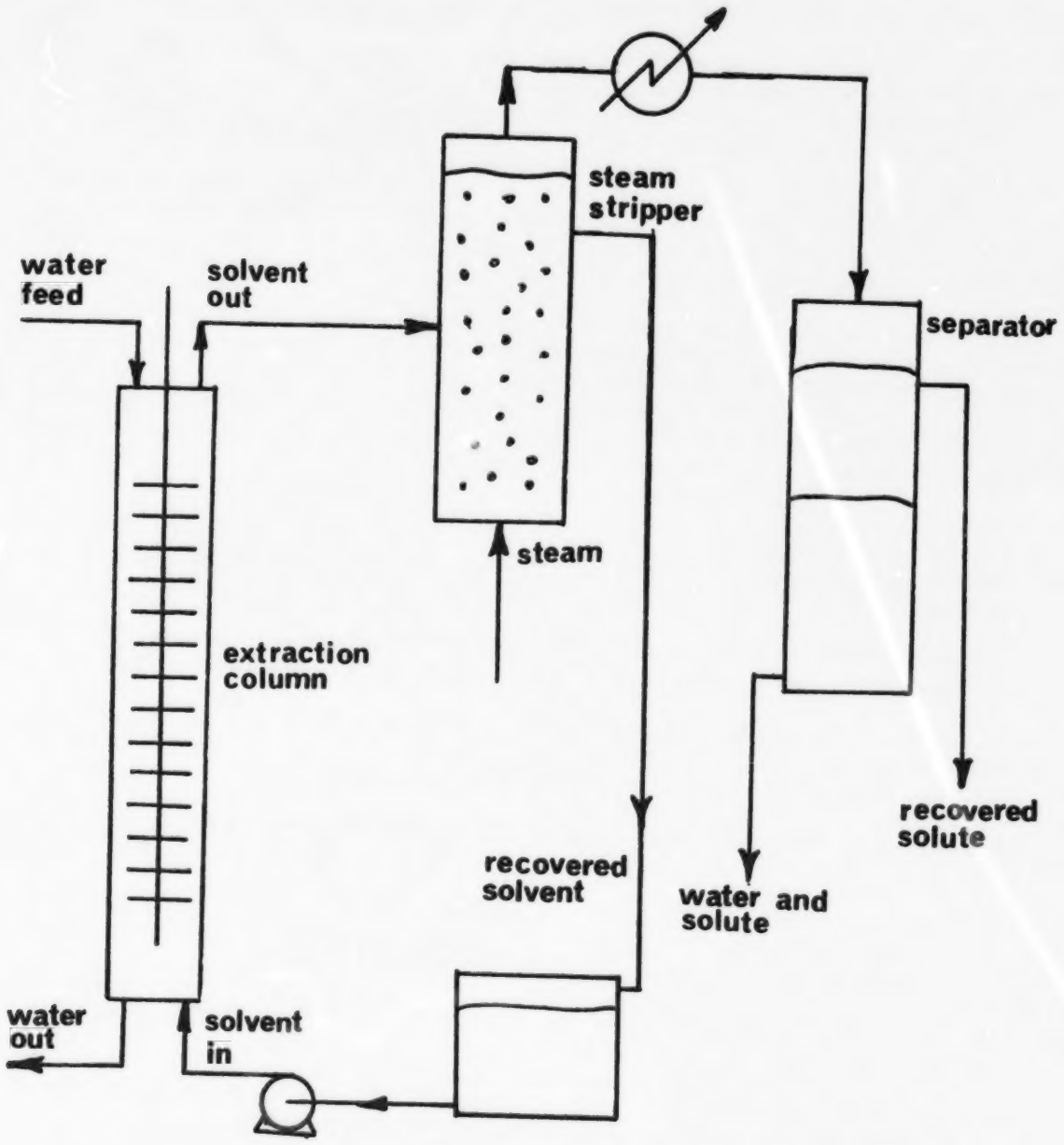

Figure 5. Present concept of mobile LE unit with solute removal

CONCLUSIONS AND RECOMMENDATIONS

Partition coefficient measurements have been made for many of the solute-solvent-water systems under consideration.

Isopar M was chosen as the test solvent for the pilot scale experiments since it is a good "broad brush" solvent. It is not toxic, not flammable and is not soluble in water.

A pilot scale RPC was operated using a water feed spiked with toluene and 1,1,2,2-tetrachloroethane and Isopar M as solvent. Removal efficiencies of approximately 90% for TECE and 99% for toluene were obtained at S/W ratios of 1/20.

Final stages of this project will include:

(i) further analysis of the partitioning thermodynamics.
(ii) further analysis of the results from the pilot scale experiments.
(iii) experimental investigation of the solute recovery options.
(iv) design of the full scale mobile LE unit.

From the results to date, it can be concluded that LE is an attractive option for the removal of hydrophobic organic compounds from water.

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ENGINEERING A MOBILE STEAM STRIPPER

by

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INTRODUCTION

Environment Canada's Environmental Emergencies Technology Division (EETD) initiated a program to deal with spills of chemical compounds such as halogenated aliphatics. The program's objective is to develop several processes that can be brought to the site of a chemical spill and used in series. No contaminated material will leave the site except the recovered concentrated chemical to be sent for reprocessing.

One of the technologies evaluated by EETD is steam stripping. CH2M HILL ENGINEERING LTD., which had successfully completed a related study for Environment Canada, was awarded the contract for the design and construction of a mobile steam stripper system. The prototype was designed and constructed in conjunction with IP Constructors Ltd. of Calgary, and was completed and delivered to Environment Canada in 1989 March. This paper describes the process of engineering a mobile steam stripper.

PROCESS DESCRIPTION

Steam stripping is a separation process that makes use of differences in the thermodynamic properties of the compounds to be separated. It is a process by which a compound that is dissolved in a liquid (usually water) is transferred to a vapour stream. The driving force for the transfer is related to a compound's vapour pressure in air relative to its solubility in water. Removal efficiency is highly dependent on Henry's Law Constant, temperature, vapour pressure, and steam-to-water ratios. An increase in any of these parameters produces an increase in removal efficiency, assuming that all other factors remain constant.

The process is carried out in a vertical three-sectioned column filled with packing to enhance vapour-to-liquid contact. Steam supplied by a boiler is introduced at the bottom and passes upward through the column. The feedwater enters at the top and flows down to the bottom. The vapour phase is always less concentrated than it would be if it were in equilibrium with the liquid with which it is in contact. Thus, the steam becomes increasingly concentrated with the compound being stripped as it travels upward and the water becomes increasingly pure as it flows downward.

The overhead vapour is condensed and a decanter tank is used to separate the insoluble compounds from the water. The water phase from the decanter is returned to the top of the column as reflux. Immiscible liquids can be collected from the decanter overflow weir or from the bottom of the decanter. When stripping miscible liquids, the waste pump can be started by a timer to waste a fixed portion of the total overhead flow. Product water is collected at the bottom of the stripping column and pumped to the product tank. Figure 1 illustrates the steam stripping process.

DESIGN CONSTRAINTS

Several constraints were set as a basis for developing the prototype. They are:

- Mobile - The complete system, excluding tankage, is to fit in a 5-ton box van of the type commonly available at rental agencies.
- Flexible - It must be able to function on a variety of compounds at varying concentrations in real situations.
- Rugged - It must withstand the rigors of transport, assembly, and disassembly.
- Easy to use - In some situations, speed of response may be critical. The equipment must be able to be unloaded and set up using rental equipment that would normally be available. It must be able to be assembled using no more than a three-person crew in not more than 24 hours. The number of utilities required is to be an absolute minimum. Foundation requirements are to be limited to a prepared gravel pad.

PROTOTYPE DESCRIPTION

A modular approach was used for construction to allow easy assembly and disassembly. The prototype consists of two separate modules: a boiler module and a process module. The boiler module provides a base for a 22-kW firetube, low pressure steam boiler and an EEMAC 3 control panel. It also provides the support of the three stripping column sections for transportation. The overall dimensions of the boiler module are 2800 mm x 1800 mm x 2100 mm (H). The overall height is to the top of the steam stripping column sections when they are secured flat on the skid for shipping. Figures 2, 3, and 4 show the front, rear, and end views of the boiler module, respectively.

The process module consists of a 305-mm diameter x 8882-mm stainless steel column, a 230 l polypropylene accumulator/ decanter tank, plate, and frame type heat exchangers, pumps,

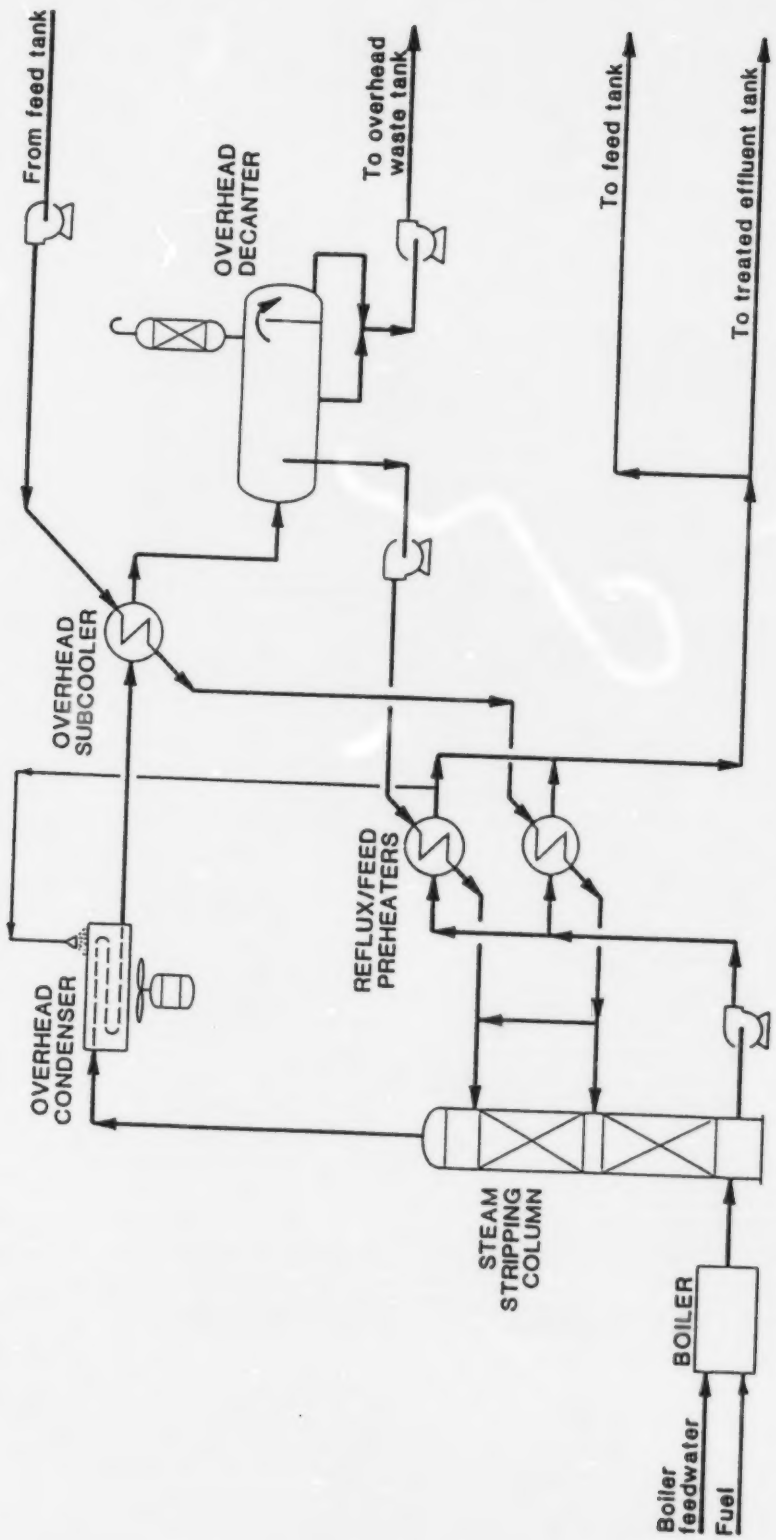


Figure 1
PROCESS FLOW SCHEMATIC

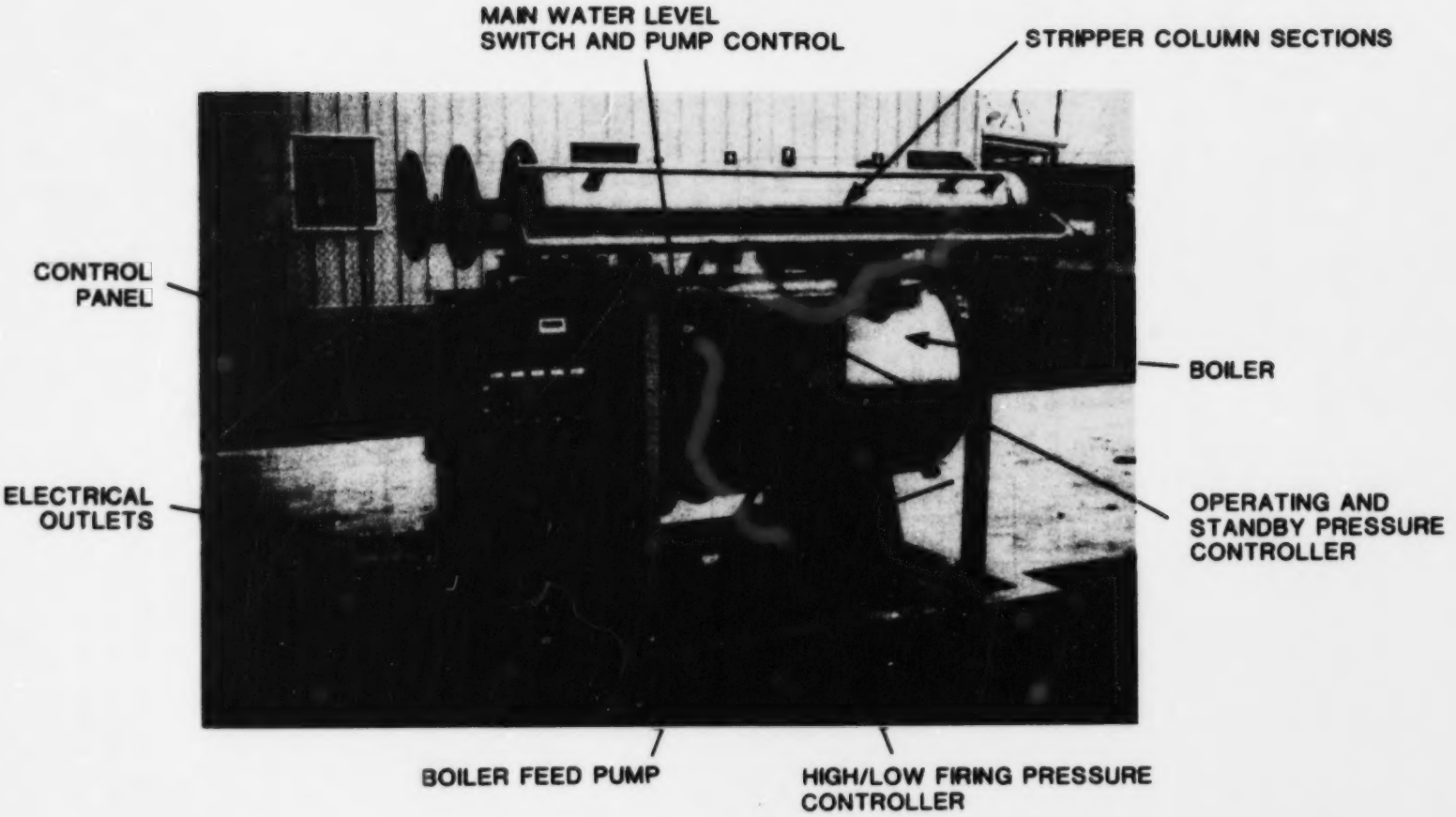
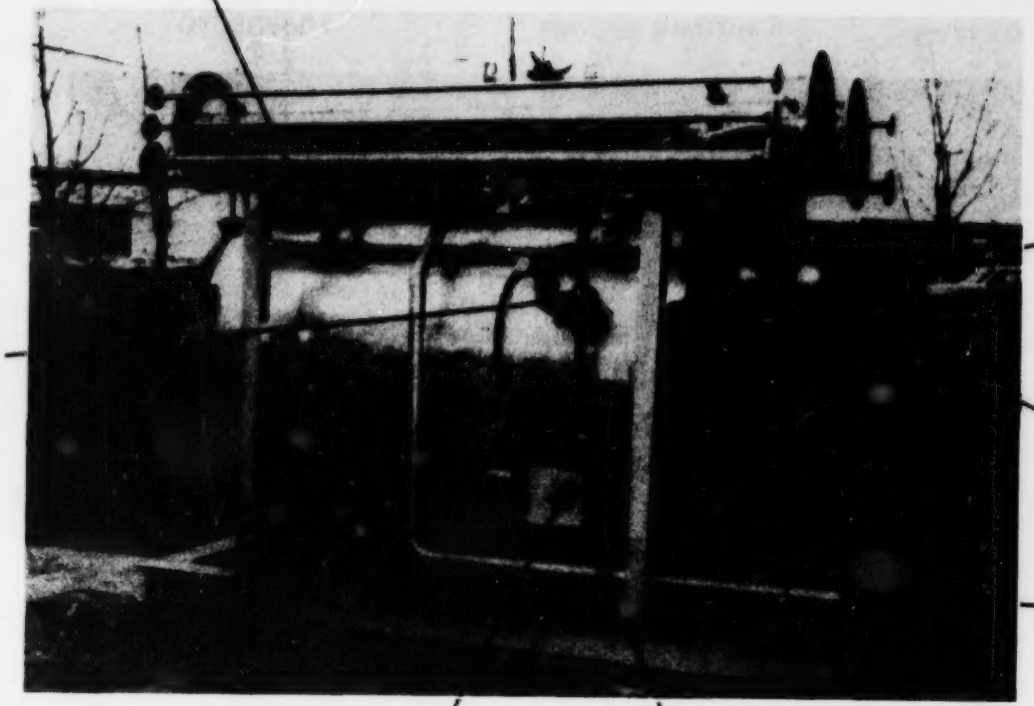


Figure 2

BOILER MODULE FRONT VIEW


SAFETY VALVE OUTLET
OIL PUMP AND BLOWER
AUXILIARY WATER LEVEL SWITCH
FLAME MONITOR/CONTROLLER "FIREYE"
STEAM OUTLET
ELECTRICAL JUNCTION BOX
OIL FILTER

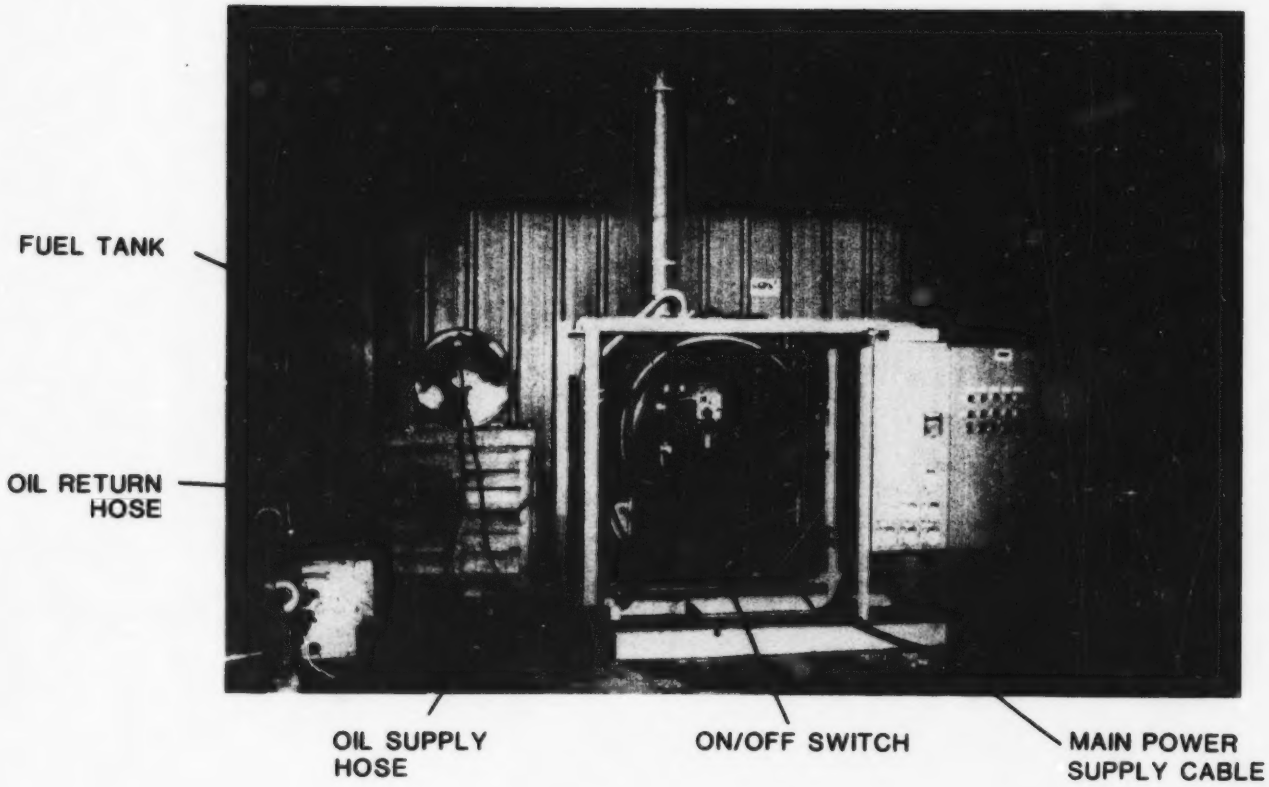


Figure 4
BOILER MODULE END VIEW

piping and instrumentation. It also provides the support for the boiler stack and the overhead condenser for shipping. The overall dimensions of the process module are 2300 mm x 1800 mm x 2050 mm (H). The overall height is to the top of the overhead condenser when it is lying flat on the skid structural support during shipping. Figures 5 and 6 show the front and end views of the process module, respectively.

Utilities required to operate the steam stripping system are diesel fuel and softened water for the boiler, and a 12 kVa electrical power source having a 220 volt, 50 amperes rating. The system is designed to treat 33.3 L/min of contaminated water. Figure 7 shows the system in operation during a test trial in the factory.

Transportation of the modules is accomplished by lifting each module into a 5-ton moving truck with a forklift, as shown in Figures 8 and 9.

Onsite assembly and disassembly can be accomplished by three people using basic power equipment (forklift, crane, tools). Startup follows by bolting the column sections onto the column base. Various hoses and cables are then connected between the process module, the boiler module, the overhead condenser, and tankage.

APPROPRIATE WASTES

In general, any compound with one or more of the following characteristics could be considered for steam stripping:

- Vapour pressure higher than water
- Sparingly soluble in water
- High activity coefficient with respect to water

Examples of candidate compounds are acetone, MEK, MIBK, methanol, ethanol, benzene, toluene, styrene, methylene chloride, ethylene dichloride, trichloroethylene, naphtha, and others.

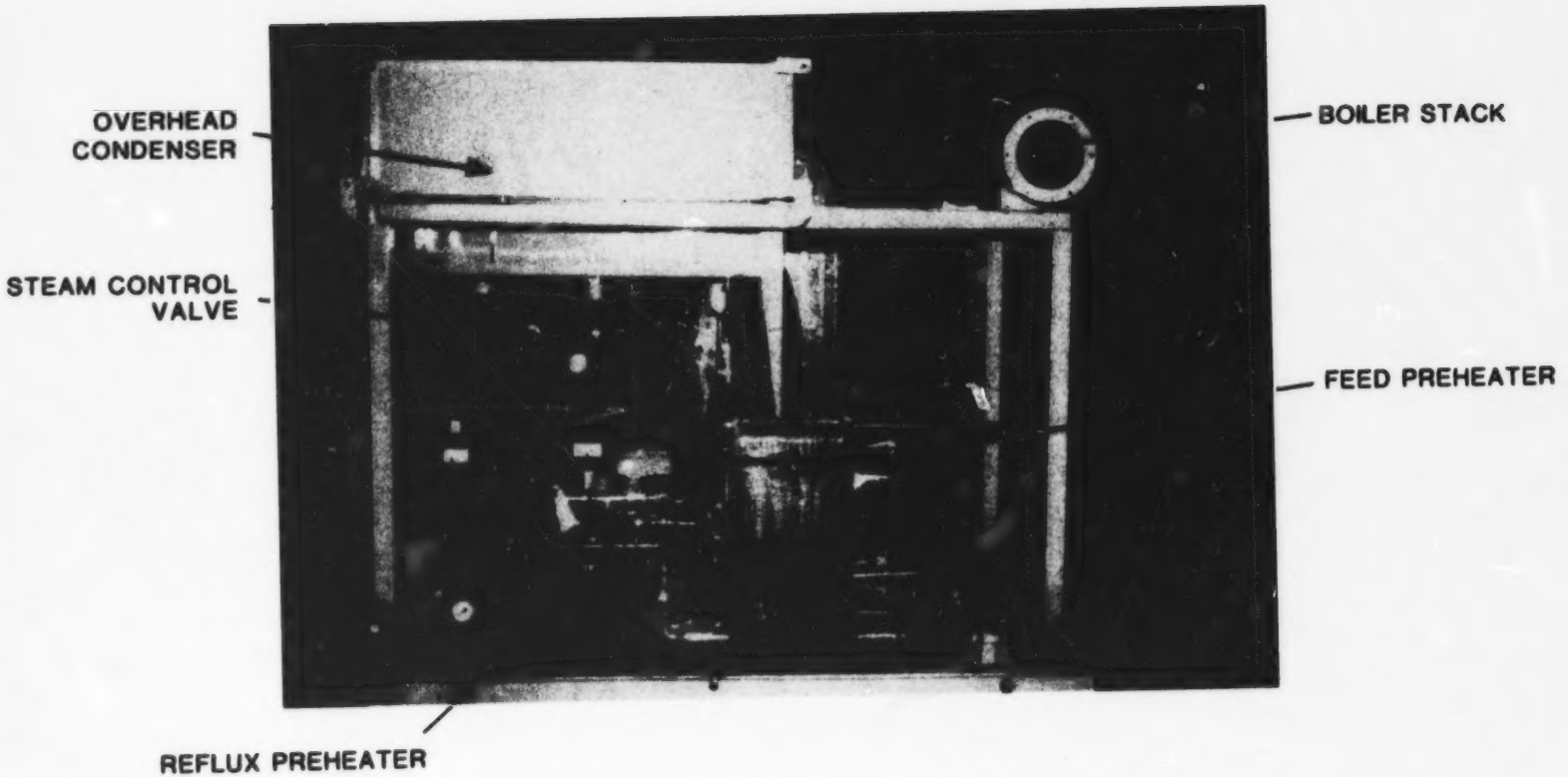


Figure 5
PROCESS MODULE FRONT VIEW

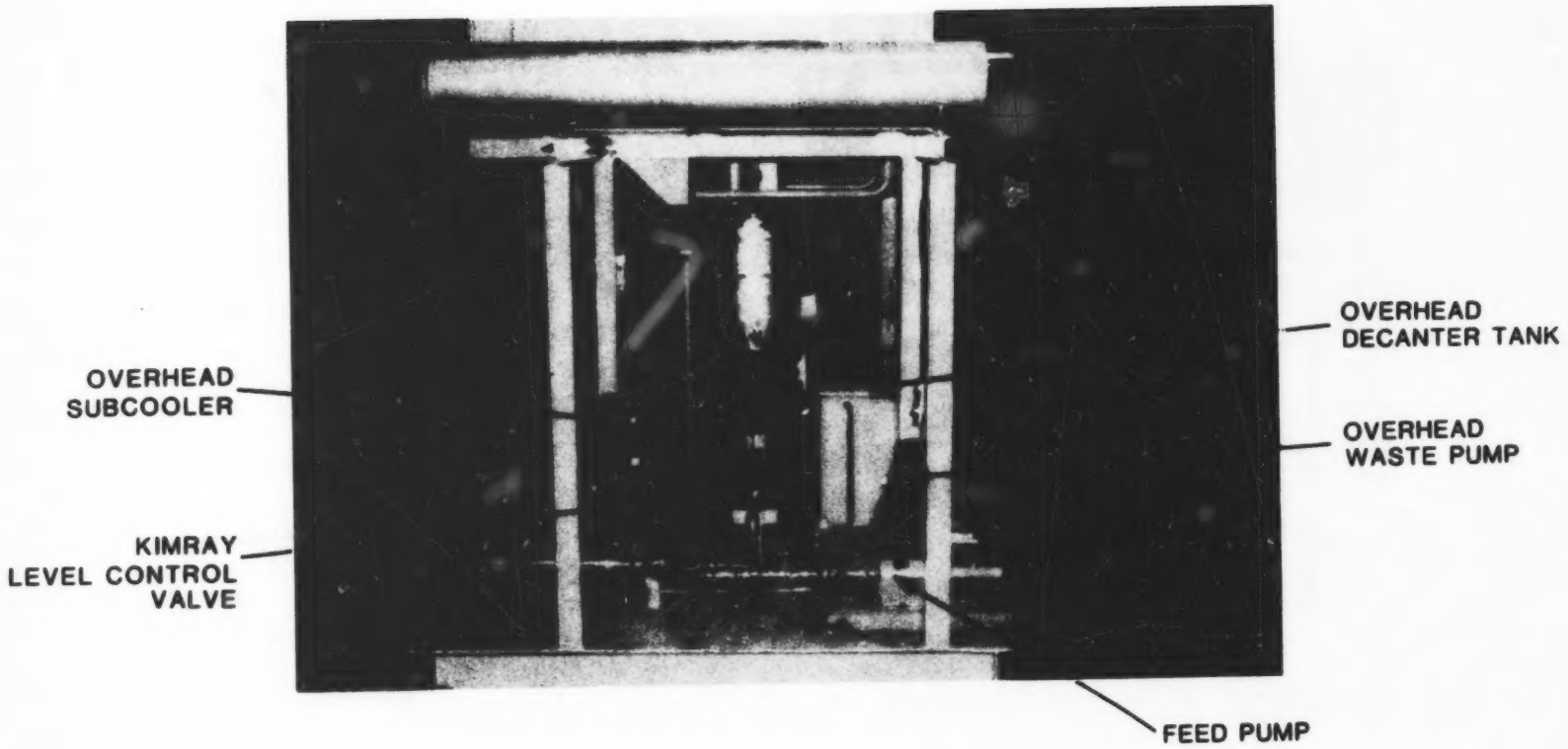


Figure 6
PROCESS MODULE END VIEW

Figure 7
STEAM STRIPPING SYSTEM IN OPERATION DURING TEST TRIAL IN FACTORY

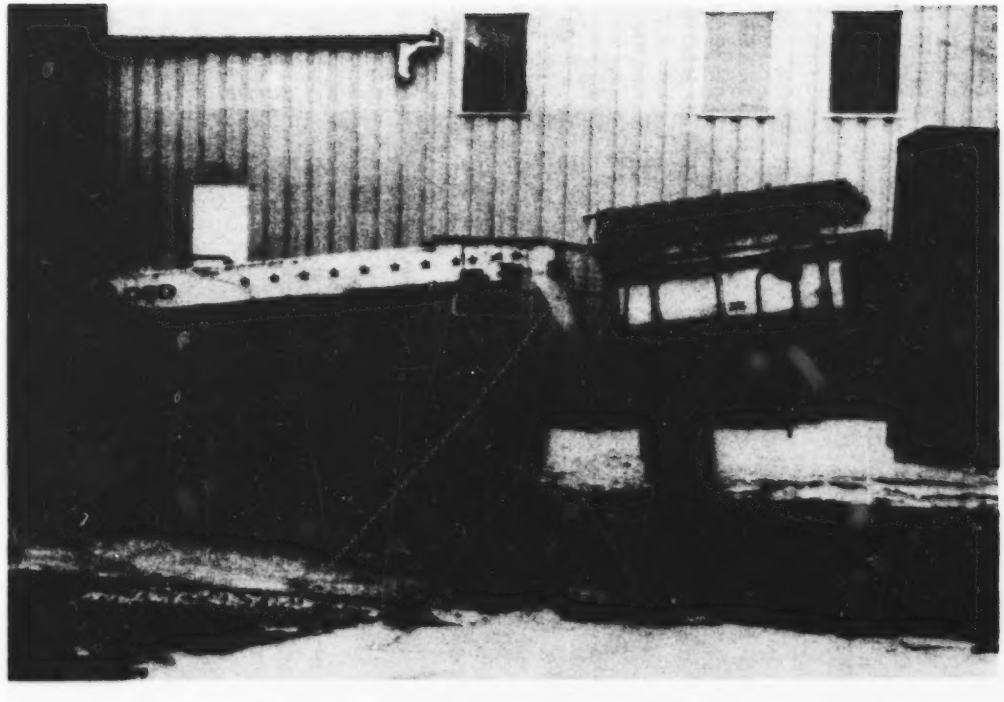


Figure 8
LOADING OF THE BOILER MODULE INTO A 5-TON TRUCK

Figure 9
TRANSPORTING THE STEAM STRIPPING MODULES WITH A 5-TON MOVING TRUCK

U.S. ENVIRONMENTAL PROTECTION AGENCY'S ENVIRONMENTAL RESPONSE TEAM'S LOGISTICAL PROBLEMS DURING EMERGENCY RESPONSE ACTIVITIES,

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INTRODUCTION:

The U.S. Environmental Protection Agency's Environmental Response Team (USEPA/ERT) was established in October 1978 to provide technical assistance to Federal On-Scene Coordinators (OSCs), Regional Response Teams (RRT), National Response Team (NRT), EPA Headquarters/Regional Offices, and other Federal/State governmental agencies in the area of environmental emergency issues such as chemical spills and hazardous waste sites.

As one of the more experienced Federal groups for handling oil spills and hazardous waste releases, the ERT is often called upon to assist the United States and Foreign Governments. The ERT can serve as a sole technical assistance source, and/or as part of larger, multi-national relief efforts.

In addition to response activities, the ERT's Health and Safety Policy provides administrative control, personnel protection equipment (PPE) selection criteria, operational guidelines, medical surveillance, and continuous Health and Safety Training. In this capacity, the ERT has furnished national and international hazardous waste activities with occupational health and safety expertise. ERT also manages the Office of Solid Waste and Emergency Response (OSWER) Integrated Health and Safety Program.

This paper describes through domestic and international case histories, logistical problems incurred by ERT during emergency activities. The paper will address those problems ranging from personnel protective clothing to equipment selection and usage. The domestic case history will address responding to an air monitoring activation of a potential hazardous trash barge that had been denied entry into both the United States (U.S.) and foreign ports. The international case histories will describe the following: Malathion Warehouse Fire, Sri Lanka; Pesticide Warehouse Spill, Eastern Africa; and the Lake Nyos disaster, Cameroon.

The objectives of this paper are to describe ERT's emergency response function for each incident and the difficulties encountered with emergency field activities. The authors hope other response personnel will find these case histories both enjoyable and informative.

PRELIMINARY EVALUATIONS:

A Preliminary Evaluation is a required part of any U.S. domestic hazardous material field activity. It is no less important for international efforts, particularly those in Third World countries. Two major elements of information that must be obtained prior to departure for a foreign response are the logistical support conditions and the necessary preventive inoculations for the region of activity.

Logistical support may range from the availability of bleach for sanitizing equipment to moving full self-contained breathing apparatus (SCBA) gear overland through roadless terrain. Even more important can be the need to know whether certain materials are even allowed into a given country. However, as shall be shown in this paper, the pre-mission information required to make logistical decisions can vary tremendously from the reality of a response situation. Deciding on equipment and making logistical arrangements can be a combination of deductive reasoning and a throw-of-the-dice.

While any general hospital can determine what preventative inoculations are required for a particular country, it is often difficult to get this information and the injections in a timely fashion. Last moment notice, as is often the case in hazardous spill situations, can require that field personnel find a knowledgeable medical center and be inoculated in the middle of the night. Such timetables can also require personnel to receive shots in countries enroute to the site of the incident. It is helpful to know what countries have little or no waiting time once emergency response staff is inoculated.

The following case histories demonstrate the wide range of preliminary information required and the difficulties with conducting emergency response activities.

GARBAGE BARGE, LONG ISLAND, NEW YORK

The ERT was requested to determine if the garbage barge contained any toxic chemicals. The barge, sailing from Long Island, New York, had been refused entry into various ports throughout the U.S. and neighboring countries due to reports that it contained toxic and medical waste. In order to determine if the barge contained these or other hazardous wastes, the barge had to be inspected and sampled. The responsibility for performing these tasks was assigned to ERT and USEPA Region II. Since EPA Health and Safety Policy clearly states that the boarding personnel be appropriately protected additional monitoring and sampling equipment was requested following a cursory investigation of the barge. This equipment needed to be on-site for use as soon as

logistically feasible. Weekend shipping requires trusting either a courier for local deliveries or buying the equipment a "seat" on the first flight out (this addresses the easy part for this particular response). Upon arrival in Key West, Florida, the equipment had to be picked up on shore and transported to the respective boats. The important factor here was communication. A miscommunication of the number of packages warranted two trips from shore to the boats. No "harm done," merely delayed actions.

The potential for "Red Bag" hospital waste being present on the barge was very real according to the information available with which to make preliminary assessment. This information would indicate a Level B entry to the barge.

Therefore, following ERT selection criteria, it was determined that the initial survey of the barge should be conducted in Level B protective equipment. However, the level of protection that was actually used during the initial survey and sampling of the barge was Level C. This downgrading of protection levels was done for the following reasons:

1. The inspection and sampling of the barge was to be performed while it was anchored approximately one mile off the coast of Key West, Florida in 100 feet of water. Personnel, inspecting the barge by binoculars at a distance of 200 feet, determined that the use of Level B might be extremely hazardous due to the fact that there was approximately a two-feet-wide path around the barge. Personnel boarding the barge would be seriously encumbered by Level B.

2. Real-time organic and inorganic vapor readings were collected by personnel while they were circling the barge in their boat. There were no readings above background from these instruments within a few feet of the barge. If any of the real-time instruments exceeded levels established in the selection criteria during the on-board survey, the inspection would be halted. Real-time instrument readings were being conducted using organic vapor monitors, organic and inorganic acid monitors, and radiation monitors. Consequently, responders had every reason to believe themselves safe boarding the barge in Level C.

MALATHION FIRE, SRI LANKA

The Sir Lanka government requested assistance from the United States Environmental Protection Agency in determining how to safely depose of 20-million pounds of malathion that was involved in a warehouse fire. The ERT was sent to Sri Lanka to provide this assistance. ERT had to determine: (1) if vapors were still being emitted, (2) if the pile was still burning, and (3) how to appropriately dispose of the waste material. The malathion was stored as wettable powder in corrugated cardboard boxes that were stacked twenty feet high. In order to perform these tasks, the ERT members would be required to hand auger holes in the pile to collect air samples and temperature readings from various locations throughout the pile.

Following the selection criteria established for determining the appropriate level of protection for workers at hazardous waste and chemical sites, it was determined that the ERT personnel required Level C protection. Level C protection was deemed appropriate because:

1. The major by-products when malathion burns are hydrogen sulfide and sulfur dioxide.
2. Malathion and its major combustion by-products have fair warning properties.
3. The burning piles were covered with sand and dirt.
4. Personnel would be performing real-time air monitoring with colormetric tubes and photoionization detector (PID).
5. The ability to refill SCBAs in Sri Lanka.

PESTICIDE WAREHOUSE, EAST AFRICA

For many years, the developed countries have been exporting and donating pesticides to East Africa in response to a need to protect fragile agrarian economy of the nations. For many reasons, excess or outdated stores of pesticides have accumulated in warehouses and stores throughout the region. Local governmental officials have characterized the problem to a great extent. However, they generally do not have the health and safety training needed for dealing with the hazardous environments that have developed around some of these storage areas as a result of leaking containers and spilled products. In the Spring of 1987, the ERT was requested to provide assessment of these situations by the U.S. Office of Federal Disaster Assistance (OFDA). The most hazardous situation of this type was at the State Fumigation and Storage Chamber in Port Sudan.

In order to control the importation of weevils and other such grain destroying pests, grain imports are often fumigated with methyl bromide upon receipt. In former times, a large, lightless, windowless, sealable warehouse was the site of this activity. Mainly because of the high degree of waste of materials, this practice was modified in Sudan by the use of fumigation "tarps." Using this simple concept, grain can be fumigated out in the open with a minimum of pesticide. In Port Sudan, the former fumigation chambers are used for storage. In particular, Ekatol (an organic-phosphate in oil), in one-gallon containers, was stored in a pile in one of these rooms. Over the course of ten years, most of the containers deteriorated, resulting in a pool of contaminated oil about 1-cm thick, covering the entire floor of the chamber. Since organic phosphates are neurotoxins, inhibiting acetol choline esterase, they pose an acute threat to humans. Respiratory and skin protection is essential. Inadequate monitoring capability, safety equipment, and training prevented authorities from assessing the hazard at this site.

With only general information to guide the responders and in accordance with ERT safety protocols, Level B protection was selected for site entry. Despite the possibility of skin penetration, Level A was not selected due to the logistical problems in the Third World associated with working at this level, not the least of which was the lack of a Level A support team. Instead, Tyvek-Saran (well taped), was selected as providing sufficient skin protection for short-term exposure. Air bottles were filled at a skin-diving shop in Khartoum, and transported to Port Sudan by private plane. Additional personnel protection equipment was standard.

Monitoring was accomplished using a hand-held photoionization detector for volatile organics, colormetric tubes for phosphoric acid esters, and a mixture of substances using the Poly test tube. Surprisingly, organophosphates were detected in small concentrations at the oil surface in spite of the age of the material. Normally, one can expect a loss of activity in a few years. These results indicated Level C with skin protection, along with ventilation of the chamber, would be suitable for cleaning up this site.

The following summarizes some of the obstacles encountered:

Upon completion of work in Sudan, arrangements were made for the equipment's return to the United States. However, the equipment was unexplainably embargoed in the Port of Sudan. We were unable to retrieve any of the gear for well over six months. Communication proved to be essential in monitoring the status of the embargo. The moment the embargo was rescinded, the gear left Sudan before another obstacle arose. Interpretation of manifests of technical equipment which most people are unfamiliar with poses a logistical problem, not only in simple identification, but also the decision to handle such items.

RESPONSE IN CAMEROON:

In September 1985, the ERT was activated by a request from OFDA to assess the residual hazards and determine the cause(s) of the Lake Nyos disaster. At the time of the activation, very little information was available from this remote area of West Africa. Despite international relief efforts (including two earlier American teams comprised of pathologists, volcanologists, and water chemists), almost no detailed data was forthcoming from the effected region. About the most definite knowledge of this situation was that 1700 people and thousands of cattle and wildlife had been killed by some gas emanating from volcanic Lake Nyos. With nothing substantial to go on, preparations took the form of a domestic response with some modifications: heavy wet-weather gear, camping equipment, Levels B and C PPE, a computer, and a generator. Altogether, the equipment was packed in twenty-one military footlockers.

OFDA policy states that the host country is responsible for the logistics of assistance teams. This includes shipping of equipment, in-country transportation, and the requirements of the visiting scientists. Any further difficulties are to be handled by the U.S. Embassy through the U.S. AID Program. However, no amount of pre-trip discussion or policy could prepare the ERT for the logistical nightmare that began from this mission's outset. No preparations for shipping the equipment had been made, and the OFDA did not advance the necessary $2500 fee for this service. OFDA personnel on-site could not assist the team. A call by an ERT colleague to the airline's New York office waived the charge. Upon arrival in Cameroon, the team was taken to meet the U.S. Ambassador, who did not appear to be aware of their mission. The Ambassador wanted to know the purpose of the mission, what further expertise the team could add to the two initial American teams still in-country, and what logistical requirements were necessary. Unfortunately, after answering the Ambassador's questions, the ERT was informed that the only means of traveling in-country were military helicopters or small Toyota 4x4s. There was little cargo capacity in either of these vehicles. Therefore, equipment selection was restricted to whatever could be backpacked or carried on one's lap. Lastly, in-country transportation went only as far as the village of Nyos below the volcano. Even if total equipment transport had been possible, the ERT would not have been able to get their equipment and PPE to the investigation point.

The following summarized the problems encountered:

1. One initial obstacle was explaining the entire manifest to a overly inquisitive Customs agent with absolutely no knowledge of what the equipment is or does... least of which is ensuring him it will not explode in the cargo hole.

2. International shipping of hazardous materials is not only a true test of patience but a lesson in attention to detail. Soliciting a vendor well versed in international shipping is only the first in many steps taken to get the necessary analytical chemicals required to Nyos, Africa. International Air Transportation Association regulations governing shipping of hazardous materials are quite explicit. However, some handlers and shippers feel their discretion is a stronger governing factor. To make a long story short, following two separate rebox and relabel attempts, despite being demonstrated to be well within the regulation, the required chemical arrived in Nyos two weeks after the work was completed.

3. While 21 pieces of "luggage" were prepared for the departing flight, the portable generator never made it back to the U.S.

CONCLUSION

The authors recommend that emergency responders establish a health and safety program consisting of the minimum policy and guidelines prior to any response activities. It should include, but not be restricted to, the following areas:

1. ADMINISTRATIVE CONTROLS: (i.e., who is responsible for doing what and when). "Office of Solid Waste and Emergency Response Integrated Health and Safety Policy for Field Activities," May 1988, (OSWER Directive NO.: 9010.15-01) U.S. EPA, Washington, D.C.
2. MEDICAL MONITORING: (i.e., who participates in this program and what is included in an examination). "Office of Solid Waste and Emergency Response Integrated Health and Safety Policy for Field Activities," May 1988, (OSWER Directive No.: 9010.15-01) U.S. EPA, Washington, D.C.
3. HEALTH & SAFETY AUDIT: (i.e., how does management know that the health and safety program is functioning properly. Audit vs. Body Count). "U.S. Environmental Protection Agency Health and Safety Audit Manuals," (OSWER Directive No. 9285.8-02) U.S. EPA, Washington, D.C.
4. HEALTH & SAFETY TRAINING: (i.e., employees must receive continuous practice, updating, and reinforcement of health and safety protocols, procedures, and requirements). "U.S. EPA/ERT Training Course Schedule," 1989, U.S. EPA/ERT, Cincinnati, Ohio.
5. PPE SELECTION CRITERIA: (i.e., what is the appropriate PPE required for the specific activity being conducted). "U.S. EPA Office of Emergency and Remedial Response Emergency, Environmental Response Team, Standard Operating Safety Guides," July 1988. (OSWER Directive No. 9285.1-02) U.S. EPA, Washington, D.C.
6. STANDARD OPERATING PROCEDURES: (i.e., are routine and/or mandatory procedures in writing). "U.S. EPA Office of Emergency and Remedial Response Emergency, Environmental Response Team, Standard Operating Safety Guides," July 1988, (OSWER Directive No. 9285.1-02) U.S. EPA, Washington, D.C.

The literature cited in this section can be obtained by writing to:

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